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A QUANTITATIVE ASSESSMENT OF THE MUTAGENS AND POLYNUCLEAR AROMATIC HYDROCARBONS IN DIESELIZED UNDERGROUND MINES

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INTRODUCTION

Diesel equipment was introduced into Canadian underground mines in the early 1950's and its use has increased markedly in the intervening years. Today a major portion of the equipment used in underground mines is powered by diesel engines. Although diesels are more convenient, safer and more economical to operate, they burn hydrocarbon fuel that releases several pollutants into the mine environment. The combustion products and unburned portions of the fuel that are added to the mine environment include particulate matter or soot which is small (mainly respirable) carbon particles, carbon monoxide, carbon dioxide, sulfur dioxide, nitrogen oxides, oxygenated hydrocarbons such as aldehydes and two classes of hydrocarbons - aliphatic (straight chain) hydrocarbons and aromatic hydrocarbons which include the class of compound known as polynuclear aromatic hydrocarbons or PAHs or PNAs (1,2).

Catalytic converters and/or increased ventilation have reduced the levels of the gaseous pollutants (CO, NO_x, SO_2 and oxygenated hydrocarbons) to safe (acceptable) levels in the mine (1). The presence of aliphatic hydrocarbons in the exhaust is not a problem because these compounds are not toxic. To date, the removal of the particulate or soot has not been completely investigated, although work to develop new filters which will remove the mainly respirable particulate in the exhaust has begun (3). The remaining pollutants in the mine atmosphere, the polynuclear aromatic hydrocarbons (PAHs or PNAs) have not been investigated to any great degree in underground mines.

The presence of PAH compounds in underground mines is of concern because several of the PAH compounds detected in the exhaust have been found to be carcinogenic in skin tests and mutagenic by Ames testing (4,5). Many of these PAH compounds have also been identified in cigarette smoke and it is believed that they are responsible for the increased incidence of lung cancer in smokers (6,7). Thus, the presence of the PAHs in the exhaust of diesels used in underground mines means that carcinogenic compounds are present in the mine air. Because the PAHs can only be carried away by the mine ventilation, all the miners working around or downstream from the diesels can be exposed to air containing PAHs. The PAHs in the diesel exhaust could lead to lung cancer because the PAHs are on the respirable sized soot particles (8) and could be drawn into and deposited in lungs. This is of special concern because other studies have shown that PAHs are retained by the body for significantly longer periods of time when they are absorbed on particulate matter (9). Thus, miners inhaling the PAHs on the respirable soot particles in the diesel exhaust would experience a prolonged contact with carcinogenic PAHs and have a greater probability of contracting lung cancer.

Recently, Westaway and co-workers (2,10,11) have developed a method for isolating and analyzing thirteen polynuclear aromatic hydrocarbons in the air in dieselized underground mines. The work in the initial study demonstrated that PAHs were present in the air in underground mines at levels significantly higher than those in the air above ground. This study also showed that the PAH concentrations were directly related to the amount of diesel activity but decreased when the amount of ventilation was increased (2,12). The work done

in the 1980-81 contract year (3,13,14) extended the initial study. Samples collected in salt mines illustrated that the PAHs are found at much larger distances from the diesel activity in the salt mines than in the nickel mines. In addition, this work suggested that blasting increases the concentrations of the PAHs found in underground mines markedly. Samples collected when different catalytic converters were installed in the exhaust system of the diesel suggested that the PAH levels in the exhaust and thus in the mine air were not changed appreciably by a PTX catalytic converter but were very different when a Dieseler III catalytic converter was used. Finally, Ames testing showed that the extract from Hi Vol samples of diesel exhaust was slightly more mutagenic when a PTX catalytic converter was used and was much more mutagenic when a Dieseler III catalytic converter was in the exhaust system of the diesel.

This study extends the earlier work. The PAH levels have been measured in four different mines in an effort to i) determine how the PAH concentrations and mutagenicity of the exhaust is affected by high concentrations of NO_2 , ii) to confirm that blasting affects the PAH levels in underground mines, iii) to determine the efficiency of the sampling method, iv) to determine whether filters that remove the diesel particulate reduce the PAH concentrations in the mine environment, v) to confirm that the Dieseler III catalytic converter increases the mutagenicity of the exhaust, and vi) to learn how different diesels and vii) different fuels influence the mutagenicity and PAH concentrations in the mine air.

RESULTS AND DISCUSSION

Testing the Efficiency of the Sampling Method

In previous work, the samples were collected by placing 8" x 10" fiberglass filters over the screen of a calibrated Hi Vol sampler. In this study the efficiency of the sampling method has been tested in several ways.

Type of Filter:- Although almost all of the samples collected in the previous studies (2,11) had been collected on fiberglass filters that were reported to be at least 99.9 percent efficient in collecting particles with a diameter as small as 0.3 microns, many researchers were beginning to collect diesel exhaust particulate on Pallflex T60A20 (teflon coated glass fiber) filters. We undertook a study to determine whether Pallflex T60A20 and glassfiber filters were equally effective in collecting the PAHs in an underground environment.

The filter comparison was carried out by collecting and analyzing several sets of Pallflex and fiberglass filters for PAHs. Each set of filters was collected on two different Hi Vol samplers which were run simultaneously within a few feet of one another. In fact, samples were collected in six different locations where the PAH concentrations ranged from low (the Total PAHs were approximately 4.5 ng/m^3) to high (the Total PAHs were approximately 500 ng/m^3) to ensure that any differences between the two filters would be detected.

An examination of the results in Table 1 suggests that the PAH concentrations are not significantly different when the samples are collected on the different filters. For example, the average Pallflex/fiberglass ratio for the Total PAHs in the six samples is 1.05 ± 0.33. The corresponding averages for the Total - pyrene and the Total Carcinogenic PAHs are 1.34 ± 0.92 and 1.88 ± 1.75, respectively. If one does not include the results from the first Pallflex filter we analyzed, i.e., from the Dieseler III, Test 1 samples, where the Total - pyrene and Total Carcinogenic PAHs are unusually large, the average Pallflex/ fiberglass ratios for the Total - pyrene and Total Carcinogenic PAHs are 0.99 ± 0.34 and 1.26 ± 0.95, respectively. These ratios are all close to unity and it would appear that the same concentrations of PAHs are found whether the samples are collected on a Pallflex or a fiberglass filter. This is even more certain when one realizes how difficult it is to obtain identical samples in side by side sampling in underground mines.

This conclusion also seems reasonable when one compares the concentrations of the individual PAHs. The results in Table 1 have been grouped into four different concentration ranges, Table 2, so that the concentrations of the individual PAHs on the two filters can be compared more easily. An examination of the results in Table 2 shows that the PAH concentrations on the Pallflex and fiberglass filters are in excellent agreement, i.e., PAHs that are present at a high concentration on one filter are at a high concentration on the other filter and vice versa. In fact, only 4 or 5 of the 67 (7%) individual comparisons show a significant

TABLE 1 - A comparison of Pallflex and Fiberglass Filters as a Collection Medium

	Concentration in ng/m^3					
	URANIUM MINE		NICKEL MINE		SUDBURY SURFACE AIR	
	Pallflex	Fiberglass	1500' Level Pallflex	1500' Level Fiberglass	Pallflex	Fiberglass
Pyrene	305	392	4.98	5.64	2.00	2.42
Fluoranthene	35.7	26.7	0.26	0.51	0.32	0.27
Benzo(a)anthracene*	31.9	37.0	0.70	2.20	0.52	1.02
Benzo(e)pyrene	56.5	49.2	0.57	0.50	0.84	0.65
Perylene	0.69	1.3	0.01	0.01	0.01	0.01
Benzo(k)fluoranthene	1.42	6.5	0.02	0.06	0.04	0.11
Benzo(a)pyrene*	1.41	3.9	0.02	0.01	0.02	0.02
Benzo(ghi)perylene*	6.69	9.9	0.18	0.15	0.09	0.07
Dibenzo(a,h)anthracene*	4.15	4.4	--	--	--	--
Dibenzo(def,mno)chrysene	0.09	0.3	0.01	0.01	0.01	0.01
Naptho(1234,def)chrysene*	10.0	6.7	0.05	0.57	0.17	0.10
Benzo(rst)pentaphene*	0.46	0.01	0.03	0.05	0.02	0.03
Total PAHs	454	538	6.82	9.69	4.04	4.70
Total-pyrene	149	146	1.84	4.05	2.04	2.29
Total Carcinogens	54.6	61.9	0.98	2.98	0.82	1.23
Pallflex/Fiberglass Ratios						
for Total PAHs	0.84		0.70		0.86	
for Total-pyrene	1.02		0.45		0.89	
for Total Carcinogens	0.88		0.33		0.67	

TABLE 1 (Cont'd)

	Concentration in ng/m^3					
	DIESELER III (Test 1)		DIESELER III (Test 2)		INTAKE AIR SAMPLES	
	Pallflex	Fiberglass	Pallflex	Fiberglass	Pallflex	Fiberglass
Pyrene	26.4	46.5	57.9	30.6	12.9	12.3
Fluoranthene	1.56	5.64	4.52	8.73	1.3	0.2
Benzo(a)anthracene*	11.0	1.31	28.7	14.8	7.8	2.4
Benzo(e)pyrene	19.3	3.57	9.77	5.46	2.8	8.1
Perylene	0.15	0.05	0.11	0.19	0.02	0.03
Benzo(k)fluoranthene	1.23	0.27	0.46	1.25	0.15	0.2
Benzo(a)pyrene*	0.74	0.12	0.28	0.65	0.08	0.03
Benzo(ghi)perylene*	3.80	1.07	1.48	1.04	1.0	0.4
Dibenzo(def,mno)chrysene	0.21	0.06	0.20	0.20	0.05	0.03
Naptho(1234,def)chrysene*	3.24	0.89	2.35	2.26	1.6	0.8
Benzo(rst)pentaphene*	0.75	0.52	0.29	0.62	0.09	0.2
Total PAHs	68.4	60.0	106	65.9	27.8	24.7
Total-pyrene	42.0	13.5	48.2	35.2	14.8	12.3
Total Carcinogens	19.5	3.90	33.1	19.4	10.5	3.9
Pallflex/Fiberglass Ratios						
for Total PAHs	1.1		1.61		1.1	
for Total-pyrene	3.1		1.37		1.2	
for Total Carcinogens	5.0		1.71		2.7	

* Carcinogenic PAHs

TABLE 2 - Comparison of the individual PAH concentrations on Pallflex and Fiberglass filters.

Concentration in ng/m^3									
PAHs at a High Concentration		PAHs at an Intermediate Concentration		PAHs at a Low Concentration		PAHs at a Concentration <1 ng/m^3			
Pallflex	Fiberglass	Pallflex	Fiberglass	Pallflex	Fiberglass	Pallflex	Fiberglass	Pallflex	Fiberglass
305	392	19.3	3.6	2.3	2.3	1.0	0.4	0.09	0.3
57.9	30.6	12.9	12.3	2.0	2.4	0.8	0.65	0.09	0.2
56.5	49.2	11.0	1.3	1.6	0.8	0.7	0.5	0.09	0.07
35.7	26.7	10.0	6.7	1.5	1.0	0.7	0.1	0.08	0.03
31.9	37.0	9.8	5.5	1.3	0.2	0.57	0.5	0.05	0.57
28.7	14.8	7.8	2.4	1.2	0.3	0.5	1.0	0.05	0.03
26.4	46.5	6.7	9.9	0.7	2.2	0.46	0.01	0.04	0.11
		5.0	5.6	0.7	1.3	0.32	0.27	0.03	0.05
		4.5	8.7	0.5	1.3	0.30	0.7	0.03	0.05
		4.2	4.4			0.3	0.6	0.02	0.06
		3.8	1.1			0.26	0.51	0.02	0.03
		3.2	0.9			0.2	0.06	0.02	0.03
		2.8	8.1			0.2	0.2	0.02	0.03
		1.4	6.5			0.18	0.15	0.02	0.01
		1.4	3.9			0.17	0.10	0.01	0.01
						0.15	0.20	0.01	0.01
						0.1	0.20	0.01	0.01
						0.1	0.05	0.01	0.01

difference between the two filters. Again, considering that it is almost impossible to collect identical samples in underground mines, it is highly probable that there are no significant differences in the PAH concentrations found on Pallflex and fiberglass filters.

Finally, it is worth noting that the Pallflex/fiberglass ratio is independent of the location of the sampler, i.e., whether the samples were collected above ground or underground or whether they were collected in highly polluted or slightly polluted air.

The results presented above indicate that the type of filter used in collecting the sample does not influence the results. In fact, this conclusion is supported by other work. Recently, both Bradow (15) and Zweidinger (16) have reported that the filters do not have a major effect on the particulate collected from diesel and gasoline powered vehicles used above ground. Zweidinger suggests that the filter effects are small because most of the particulate is collected (falls) on particulate that had already been collected on the filter. Only a small amount (a monolayer) of the particulate is actually in contact with the filter.

Collection Efficiency:- While the above work removed the concern associated with comparing the results obtained using Pallflex and fiberglass filters, it did not show that the PAHs in the air were being collected quantitatively on the filter. We had worried about this problem because we had found much smaller (approximately one-tenth) amounts of PAHs when we collected the particulate at high temperatures, i.e., close to the exhaust pipe of a

diesel (17). This suggested that the PAHs either passed through the filter as a vapour or were desorbed from the particulate as more hot air was drawn through the filter.

In spite of these concerns, we had not spent any time trying to determine the efficiency of the collection because i) all our samples were collected at low (the normal mine) temperatures where the high boiling PAHs should exist as aerosols or solid particles and not in the vapour state, and ii) because any desorption from the particulate would be expected to be small at normal mine temperatures. Moreover, iii) we had found that the PAHs were difficult to remove from the particulate collected in dieselized underground mines, i.e., it took much longer to extract the PAHs from the particulate collected in dieselized mines than it did to remove the PAHs from the particulate collected above ground (2,10). This suggested that the PAHs were strongly adsorbed on the diesel particulate and that the affinity of the particulate for the PAHs was high. This in turn, suggested that the collection efficiency was high. Another fact iv) which suggested that the collection efficiency was high was that diesel particulate could adsorb up to 1000 times more benzo(a)pyrene than the amount normally found on diesel particulate (18). The high affinity of the PAHs and the diesel particulate, the low temperature and the great capacity for adsorbing benzo(a)pyrene and presumably other PAHs, suggested that the PAHs would be associated with the diesel particulate and that it would be collected very efficiently on the filter at normal mine temperatures.

However, some recent experiments, (<u>vide infra</u>) suggested

that the collection of the PAHs in the mine air might be much less quantitative than we had expected. As a result, we attempted to determine the efficiency of the Hi Vol method for collecting PAHs in three separate experiments.

The first set of experiments involved collecting two Hi Vol samples simultaneously on two different Hi Vols at the same location above ground in Sudbury. One sample was collected for 6 hours while the other sample was collected for 24 hours. An examination of the results in Table 3 shows that the concentrations of the individual PAHs are greater in the 6 hour sample. In fact, the PAHs are between 1.0 and 6.5 times higher in the 6 hour sample. In addition, the Total PAHs are 3.2 times higher, the Total - pyrene is 4.0 times higher and the Total Carcinogenic PAHs are 3.4 times more concentrated in the 6 hour sample. The higher concentrations in the 6 hour sample could have arisen because some of the PAHs originally collected on the filter, vapourized (were lost) when more air was drawn through the filter and/or because the PAH concentrations were lower in the 18 hours after the 6 hour sample had been collected. The latter explanation seemed less likely because the 6 hour sample was collected during the afternoon when the PAH concentrations should be low. The 24 hour sample was collected overnight and in the morning when it was colder. This meant that more furnace oil and/or wood was burned during the 24 hour sampling period than during the 6 hour sampling period and since both these materials add PAHs to the atmosphere when they are burned, higher PAH concentrations would have been expected in the 24 hour sample. In addition, the

TABLE 3 - PAH Concentrations in the Sudbury Air

	Concentration in ng/m^3 SUDBURY AMBIENT AIR	
	6 Hour Sample	24 Hour Sample
Pyrene	6.01	2.42
Fluoranthene	0.63	0.27
Benzo(a)anthracene*	2.87	1.02
Benzo(e)pyrene	3.76	0.65
Perylene	0.01	0.01
Benzo(k)fluoranthene	0.38	0.11
Benzo(a)pyrene*	0.15	0.02
Benzo(ghi)perylene*	0.44	0.07
Dibenzo(def,mno)chrysene	0.01	0.01
Naptho(1234,def)chrysene*	0.18	0.10
Benzo(rst)pentaphene*	0.10	0.03
Total PAHs	15.0	4.70
Total-pyrene	9.01	2.28
Total Carcinogens	4.23	1.23

* Carcinogenic PAH

traffic was heavier in the evening and in the morning and again, one would expect that the PAH concentrations would be higher in the 24 hour sample. Since higher concentrations of PAHs were expected in the 24 hour samples, the results suggest that PAHs are being lost (are desorbed or evaporated) when more air is drawn over the particulate that had collected on the filter in the early stages of the sampling.

This suggestion was confirmed in a second experiment. Three Hi Vol samples were collected on fiberglass filters at the same location above ground in Sudbury. A 6 hour and an 18 hour sample were collected sequentially on one Hi Vol sampler while a 24 hour sampler was being collected on a second Hi Vol sampler. Thus, the 6 and 18 hour samples were collected in the same air as the 24 hour sample and should, therefore, contain the same total amount of PAHs.

A comparison of the concentrations of the individual PAHs shows that the concentrations generally decrease as the sampling time is increased, Table 4. In fact, all but three of the PAHs are less concentrated in the 24 hour sample than in the 18 hour sample and all of the PAHs in the 24 hour sample are present at much lower concentrations than they are in the 6 hour sample. The same trend is observed when the Total PAHs, the Total - pyrene and the Total Carcinogenic PAHs are compared. Because the PAH concentrations in the 24 hour sample are lower than those in either the 6 hour or the 18 hour samples, one must conclude that PAHs are being lost from the filter during the sampling.

The loss of PAHs during the sampling has been demonstrated

TABLE 4 - PAH concentrations in air samples collected simultaneously over a 24 hour period

	Concentration in ng/m^3 SUDBURY AMBIENT AIR			
	6 Hour Sample	18 Hour Sample	24 Hour Sample	24 Hour Calculated
Pyrene	14.7	6.77	6.26	8.77
Fluoranthene	1.50	0.88	0.61	1.04
Benzo(a)anthracene*	1.61	1.05	0.60	1.19
Benzo(e)pyrene	4.95	3.57	2.74	3.91
Perylene	0.11	0.10	0.08	0.10
Benzo(k)fluoranthene	0.83	0.79	0.60	0.80
Benzo(a)pyrene*	0.37	0.25	0.26	0.28
Benzo(ghi)perylene*	1.06	0.30	0.63	0.49
Dibenzo(a,h)anthracene*	0.81	0.18	0.16	0.34
Dibenzo(def,mno)chrysene	0.11	0.06	0.06	0.07
Naptho(1234,def)chrysene*	3.59	0.59	1.05	1.34
Benzo(rst)pentaphene*	0.28	0.14	0.09	0.18
Total PAHs	29.9	14.9	13.1	18.5
Total-pyrene	15.2	7.91	6.87	9.73
Total Carcinogens	7.72	2.51	2.78	3.81

* Carcinogenic PAHs

in two other ways. First, the weight of each PAH on the 6 hour filter was added to the weight of that PAH on the 18 hour filter to give the total amount[1] (weight) of each PAH collected in 24 hours. The total weight of each PAH was then divided by the volume of air that had been sampled in the 24 hour sample. This gave the PAH concentrations for a hypothetical 24 hour sample, column 4, Table 4. If PAHs were not lost during the sampling, the PAH concentrations in the 24 hour sample and the calculated 24 hour sample should be identical. In fact, the concentrations of all but one of the PAHs (benzo(ghi)perylene) are much lower in the 24 hour sample, i.e., the concentrations of the individual PAHs in the 24 hour sample are between 49 and 93 percent of the concentrations in the hypothetical sample. The same effect is observed when one looks at the totals for the two samples. The total PAHs, the Total - pyrene and the Total Carcinogenic PAHs in the 24 hour sample are only 71%, 71%, and 73%, respectively of the corresponding totals in the hypothetical 24 hour sample. Again, it is clear that a significant portion of the PAHs were lost (desorbed) from the filter during the sampling.

In fact, the losses are greater than those estimated by the above calculations because significant amounts of PAHs would have been lost when the 18 hour sample was collected. The extent of the loss due to desorption of PAHs from the particulate on the filter can be estimated from the Total PAHs versus sampling time plot, Figure 1. The correlation coefficient of 0.97 for the Total

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[1] The weights of each PAH were adjusted to correct for the small differences in the volumes of air sampled.

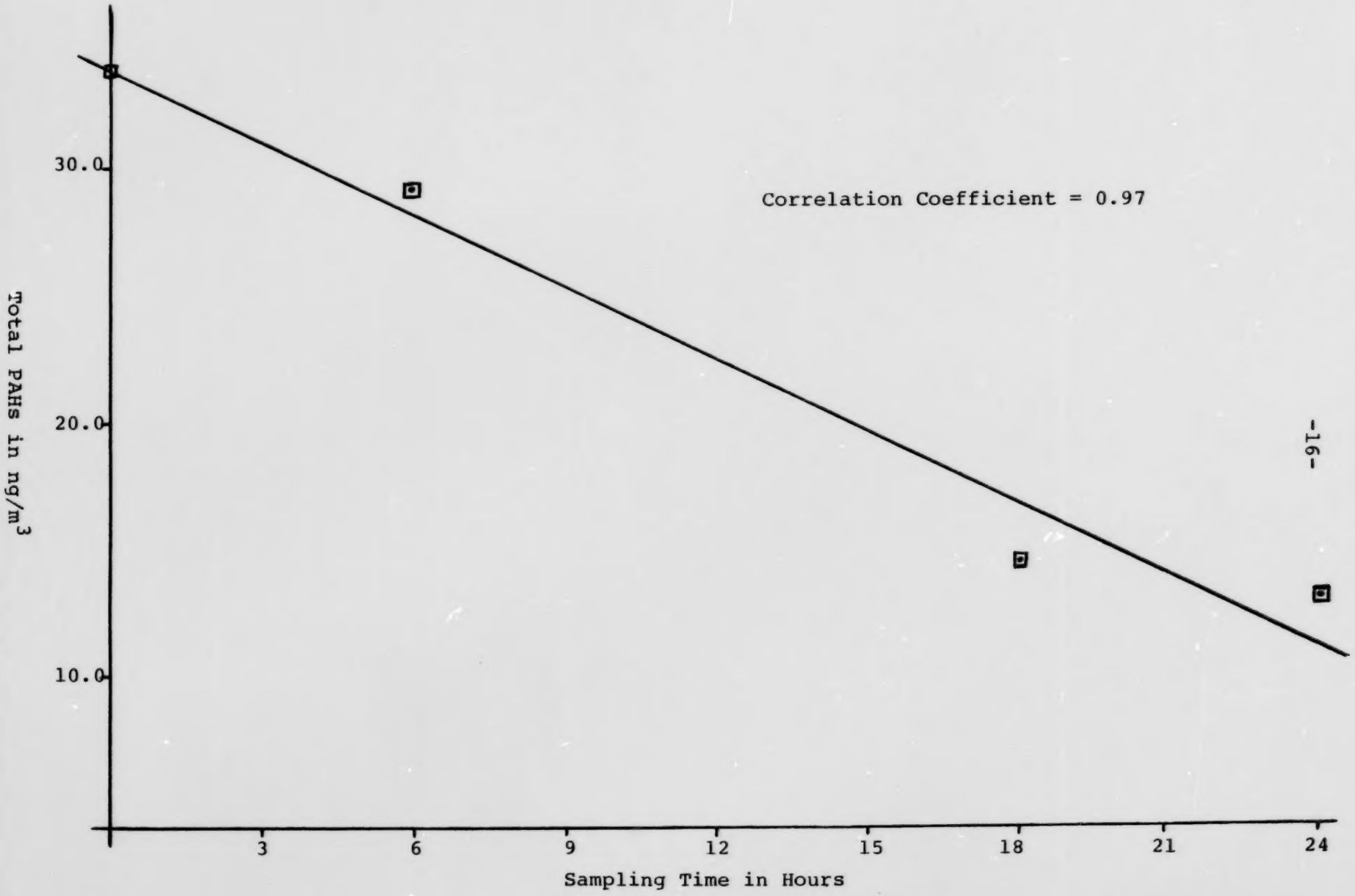


Figure 1. Concentration of PAHs versus Sampling Time, Sudbury Air, February 1982.

PAH versus sampling time curve indicates that these two factors are linearly related. The correlation coefficients of 0.98 and 0.92 for the Total - pyrene and the Total Carcinogenic PAHs versus sampling time plots also confirm that the PAH concentrations decrease linearly with sampling time. In fact, one can use the linear relationship between the PAH concentration and the length of the sampling period to calculate the PAH concentration at time t=0, i.e., the concentration one would expect if no PAHs were lost (desorbed) in the sampling. This analysis indicates that 14% of the PAHs have been lost in the first 6 hours, 58% are lost in 18 hours and 63% of the PAHs have been lost when the sample was collected for 24 hours.

Although these results clearly demonstrate that PAHs are lost (desorbed from the particulate) during the sampling, it does not enable us to indicate the magnitude of the effect in underground sampling. The problem arises because several factors should influence the amount of PAHs lost during sampling.

One factor suggests that the losses would be even greater in underground sampling. The three samples used in this experiment were collected between -7 and -18°C.. The rate of desorption would be small at these temperatures because the vapour pressure of the PAH decreases with decreasing temperature. This would mean that more PAHs would be lost underground where the temperature is less than or equal to 17°C..

Two other factors suggest that the loss of PAHs may not be as great a problem in underground sampling. First, the PAHs are adsorbed onto diesel particulate more strongly than they are

adsorbed onto the particulate collected on the surface (2,10). This stronger attraction to diesel particulate would mean that the losses due to desorption of the PAHs might be smaller in samples collected in underground mines. The second factor which reduces the concern is that the sampling times are usually less than 3 hours in underground mines. This also means that smaller percentages of PAHs would be lost in the sampling.

Unfortunately, time did not permit us to determine whether the losses of PAHs in underground sampling are greater or smaller than those found on the surface.

The third experiment in this series demonstrates that the affinity of diesel particulate for PAHs is not as great as we had thought (10). In this experiment, two Pallflex T60A20 filters were collected simultaneously, i.e., behind one another on the same Hi Vol, in a mine where the PAH concentrations were very high. Although the back filter was very light in colour and did not contain very much diesel (black) particulate, it did contain PAHs. In fact, the results in Table 5 show that the PAHs on the back filter represent a significant portion of the PAHs on the front filter. For example, the individual PAHs on the back filter equal between 17% and 195% of the PAHs on the front filter. In addition, the Total PAHs, Total - pyrene and Total Carcinogenic PAHs on the back filter are equal to 38%, 37% and 41% respectively, of the corresponding total concentrations on the front filter.

These results clearly demonstrate that the PAHs are not totally absorbed on diesel particulate in the mine but can be present in other forms. For example, it is not known whether the

TABLE 5 - Concentrations From Two Filters Collected Simultaneously on a Hi Vol Filter

	Concentration in ng/m^3	
	Front (First) Filter	Back (Second) Filter
Pyrene	305	118
Fluoranthene	35.7	5.95
Benzo(a)anthracene*	31.9	10.6
Benzo(e)pyrene	56.5	26.0
Perylene	0.69	0.22
Benzo(k)fluoranthene	1.42	0.77
Benzo(a)pyrene*	1.41	0.61
Benzo(ghi)perylene*	6.69	2.53
Dibenzo(a,h)anthracene*	4.15	0.83
Dibenzo(def,mno)chrysene	0.09	0.18
Naptho(1234,def)chrysene*	10.0	6.96
Benzo(rst)pentaphene*	0.46	0.76
Total PAHs	454	173
Total-pyrene	149	55.4
Total Carcinogens	54.6	22.3

* Carcinogenic PAHs

PAHs on the back filter are found because a) they pass through the diesel particulate on the front filter as a vapour without being adsorbed and/or b) whether the PAHs are desorbed (lost) from the diesel particulate on the front filter as more air is drawn through the filter. Whether explanation a, b or a and b are correct, one must conclude that PAHs are lost during Hi Vol sampling and that the affinity of diesel particulate for PAHs, i.e., the ability to either trap and/or retain PAHs, is much less than had been anticipated. This has serious implications for those attempting to reduce the PAHs in the mine air (see section on "Exhaust Filters and the Mine Environment"). Obviously, the Hi Vol sampling technique does not enable one to obtain accurate concentrations of the PAHs in dieselized underground mines. It is worth noting in this regard that the ability of these filters to trap PAHs is far from quantitative since at least 40% of the PAHs in the mine air were not collected on the front (a single) Pallflex T60A20 filter. In addition, if the losses are due to desorption of the PAHs, the effect is extremely large because this sample was only collected for 16 minutes. Finally, it is worth noting that the PAH concentrations are equal whether the samples were collected on Pallflex or fiberglass filters. Thus, the collection efficiency is low for both filters.

Present reports (19,20) indicate that this phenomenon has been found by other workers. Although the temperature of the filter was higher (52°C) in one of these studies than in our experiment (approximately 18°C) very large amounts of PAHs were not retained by the filter. For example, the ratio of (the total

concentration of a PAH / the concentration of that PAH on the filter) was as high as 56 for the low molecular weight PAHs. Smaller ratios were observed for the higher molecular weight PAHs. However, it has not been established whether all the PAHs were retained in any of the experiments and thus, the losses may be even greater than these other workers found. Finally, this work only shows that Hi Vol filters do not trap PAHs quantitatively, and does not indicate whether the PAHs pass through the filter in the vapour state and/or are desorbed from the diesel particulate when more exhaust is sampled. In any case, it is clear that Hi Vol sampling does not collect the PAHs quantitatively. This means that the PAH results and Ames results are inaccurate because they have been carried out on incomplete samples. However, the results from PAH and Ames testing should still be useful if they have been used in a relative or comparative manner.

The Concentrations of PAHs in Dieselized Underground Mines

Hi Vol samples for PAH analysis and mutagenic screening using the Ames test, have been collected in several different mines in order to learn how i) different diesels, ii) different exhaust treatment devices iii) different fuels and iv) different mining operations affect the air quality in underground mines.

Background PAH Levels:- In order to assess the effect of a particular mining operation or piece of equipment on the PAH concentration in the mine air, one has to know the PAH concentrations in the air entering the test site in the mine. In the 1980-81 study

and the early stages of the 1981-82 study, Hi Vol samples were collected in the fresh air raises at the entrance to the test area. A PAH analysis gave the background PAH levels for the test. Although this approach was scientifically sound, it increased the number of samples markedly and was therefore, very time consuming and expensive. In addition, the samples collected in the fresh air raise gave background PAH levels which seemed to be too high. For example, the average Total PAHs, Total - pyrene and Total Carcinogenic PAHs found in the fresh air raises underground during the 1980-1982 period were 32.7 ± 20.7, 13.0 ± 6.15 and 4.90 ± 2.71 ng/m^3, respectively, Table 6. Even if the four PAH concentrations which are out of line with the others, i.e., the pyrene concentrations in samples 3,4 and 8 and the benzo(a)-pyrene concentration in sample 8, are not used in calculating the averages, the average Total PAHs, Total - pyrene and Total Carcinogenic PAHs are still 21.6 ± 5.7, 11.5 ± 4.3 and 4.90 ± 2.7 ng/m^3, respectively.

The corresponding totals for a large city, Windsor, Ontario, where the PAH concentrations should have been high, were only 5.50, 0.92 and 0.45 ng/m^3. The totals for a small rural town, Pugwash, Nova Scotia, were only 3.95, 1.62 and 0.90 ng/m^3. Thus, the PAHs in the fresh air raise underground were much higher than those above ground. As a result, several experiments were designed to i) determine the PAH concentrations in the Sudbury air and ii) to learn why the PAH levels were so high in the fresh air raises.

The results in Table 6 suggest that the average Total PAHs,

TABLE 6 - PAH concentrations in the fresh air raise near the worksite in the mine

	Concentration in ng/m^3									
	1	2	3	4	5	6	7	8	9	10
Pyrene	12.3	4.71	36.7	29.1	9.69	13.6	12.9	54.3	9.17	14.0
Fluoranthene	0.16	0.43	0.76	1.60	1.24	0.85	1.26	1.22	0.54	1.39
Benzo(a)anthracene*	2.37	1.17	3.09	3.75	2.73	0.78	7.81	0.41	1.66	0.51
Benzo(e)pyrene	8.11	5.72	8.14	4.11	8.41	3.92	2.83	19.3	1.60	3.17
Perylene	0.03	0.03	0.10	0.03	0.11	0.17	0.02	0.10	0.03	0.06
Benzo(k)fluoranthene	0.16	0.60	0.98	0.28	0.53	0.97	0.15	0.67	0.17	0.17
Benzo(a)pyrene*	0.03	0.07	0.51	0.14	0.54	0.60	0.08	0.38	0.06	0.17
Benzo(ghi)perylene*	0.44	0.17	1.48	0.54	2.65	1.91	0.97	0.80	0.28	0.22
Dibenzo(a,h)anthracene*	0	0	0	0	0	0	0	0	0	0
Dibenzo(def,mno)chrysene	0.03	0.05	0.09	0.01	0.09	0.25	0.05	0.10	0.02	0.03
Naptho(1234,def)chrysene*	0.83	0.34	1.92	1.23	0.50	0.36	1.57	2.76	1.13	0.56
Benzo(rst)pentaphene*	0.17	0.11	0.15	0.13	0.17	0.13	0.09	0.44	0.05	0.07
Total PAHs	24.7	13.4	54.0	40.9	26.7	23.5	27.7	80.5	14.7	20.4
Total-pyrene	12.3	8.70	17.2	11.8	17.0	9.94	14.8	26.2	5.54	6.35
Total Carcinogens	3.85	1.86	7.16	5.79	6.59	3.78	10.5	4.78	3.18	1.54
Sampling Time (Hr)	4.25	4.6	3.55	2.4	4.9	5.6	4.3	2.6	3.2	3.2

* Carcinogenic PAHs

Total - pyrene and Total Carcinogenic PAHs in the fresh air raises underground are probably near 21.6, 11.5 and 4.9 ng/m^3, respectively. The next step was to determine the average PAH levels on the surface and to confirm that the PAH concentrations really were higher in the fresh air raises. Table 7 gives the PAH concentrations at three different locations on four different days above ground in Sudbury. The sampling times were almost identical and thus the losses due to desorption of the PAHs during the sampling would be almost identical (vide supra). This means that the results can be compared with some confidence. Moreover, the sampling times above ground are virtually identical to those used in collecting the samples in the fresh air raises underground and thus, the surface and underground samples can also be compared directly.

The most obvious conclusion is that the PAH concentrations vary markedly from location to location and day to day. For example, the ratio of the (most polluted/least polluted) sample is 13/1 for the Total PAHs, 16/1 for the Total - pyrene and 14/1 for the Total Carcinogenic PAHs. Obviously factors such as the location and the weather play a major role in determining the PAH concentrations at a particular sampling site. It is unfortunate that the PAH levels cover such a wide range because it means that there is no reliable average background level of PAHs. This means that the background PAH level should really be determined in every experiment.

Although there are large variations in the individual samples, the average Total PAHs, Total - pyrene and Total

TABLE 7 - The PAH concentration in Sudbury air Concentration in ng/m^3

	Feb. 20/81 SOUTH RESIDENTIAL	Oct. 12/81 SOUTH RESIDENTIAL	Feb. 8/82 NORTH-WEST INDUSTRIAL	Sept.21/81 SOUTH-WEST INDUSTRIAL
Pyrene	14.7	6.01	19.6	2.00
Fluoranthene	1.50	0.63	5.28	0.32
Benzo(a)anthracene*	1.61	2.87	3.82	0.52
Benzo(e)pyrene	4.95	3.76	12.4	0.84
Perylene	0.11	0.001	0.56	0.01
Benzo(k)fluoranthene	0.83	0.38	2.89	0.04
Benzo(a)pyrene*	0.37	0.15	1.31	0.02
Benzo(ghi)perylene*	1.06	0.44	2.13	0.09
Dibenzo(a,h)anthracene*	0.81	0	2.67	0
Dibenzo(def,mno)chrysene	0.11	0.01	0.30	0.01
Naptho(1234,def)chrysene*	3.59	0.68	1.83	0.17
Benzo(rst)pentaphene*	0.28	0.10	0.03	0.02
Total PAHs	29.9	15.0	52.8	4.04
Total-pyrene	15.2	9.02	33.2	2.04
Total Carcinogens	7.72	4.23	11.8	0.82
Sampling Time (Hr)	6.3	5.7	4.7	6.3

* Carcinogenic PAHs

Carcinogenic PAHs can be calculated for the 4 samples we have analyzed. When this is done, the averages are 25.4, 14.9 and 6.1 ng/m^3, respectively. These values are obviously too high. In fact, they are higher than the corresponding averages in the fresh air raises underground. A more reasonable estimate of the average PAH concentrations above ground in Sudbury is obtained by averaging the three less polluted samples. If this is done, the average Total PAHs, Total - pyrene and Total Carcinogenic PAHs in Sudbury air are 16.3, 8.8 and 4.3 ng/m^3, respectively. It is interesting to compare these averages with the results from the fresh air raises, the air above other mines and the values reported for Sudbury air by Katz and co-workers. These comparisons suggest that these average above ground PAH levels are reasonable.

The PAHs in the surface air are slightly greater than those found in Windsor and Pugwash. For example, when the PAH concentrations found in the air in Windsor and Pugwash are corrected to a 6 hour sampling time using the linear relationship suggested by Figure 1, the Total PAH concentrations are 12.5, 2.1 and 1.0 ng/m^3 at Windsor and 9.1, 3.6 and 2.0 ng/m^3 at Pugwash. Thus, the Sudbury air has approximately 1.3 times the Total PAHs found at Windsor and approximately twice the Total PAHs found at Pugwash. Although it is not surprising that the PAH concentrations at Sudbury are greater than those at Pugwash, it is surprising that the PAHs at Sudbury are present in higher concentrations than those at Windsor. We do not know

why this should be the case because the air entering the mine in Sudbury normally comes over open country, i.e., from the south-west or the north before it enters the city or the mine. However, PAHs must be higher in Sudbury because three of the four samples have higher concentrations of PAHs than Windsor or Pugwash. In any case, the three-sample average PAH concentrations in Sudbury air are not radically different from those found in other Canadian cities and therefore seem to be reasonable.

The PAH concentrations in Sudbury air can also be compared with those reported for Sudbury air by Katz et al.. Katz and co-workers measured the concentrations of 8 PAHs in Sudbury air. The experimental procedure used by Katz and co-workers would underestimate the PAH concentrations in Sudbury air for two reasons. First, their samples were collected over a 24 hour period and secondly, the samples were stored for several months at room temperature before they were analyzed. If the average and maximum Total PAHs reported by Katz et al. are corrected to a 6 hour sampling time using the correction factor we found for Sudbury air, their values are close to the averages we found for the same 8 PAHs. For example, the corrected average Total PAHs and the maximum Total PAHs reported by Katz et al. are 6.11 and 10.7 ng/m^3. Our average value for Sudbury air is 6.27 ng/m^3 or 1.03 times Katz's corrected value. The maximum concentrations also agree well. Our maximum Total PAHs was 12.1 ng/m^3 whereas, that reported by Katz et al. was 10.7 ng/m^3. Thus, Katz's corrected values and our estimate based on three of the four samples, are in excellent agreement.

The reasonably good agreement between the "best guess" average PAH concentration for Sudbury air and the values found in Windsor and Pugwash and by Katz's group, lead the authors to believe that the average Total PAHs in Sudbury air is close to 16.3 ng/m^3 and that the Total Carcinogenic PAHs is approximately 4.3 ng/m^3.

Once a reliable estimate of the PAHs in Sudbury air had been obtained, we were able to compare the PAH concentrations in the air on surface with that in the fresh air raise underground. This comparison is best shown by the ratios of the average Total PAHs, average Total - pyrene and average Total Carcinogenic PAHs in the fresh air raise to the corresponding totals above ground. The ratios are $\frac{21.6}{16.3} = 1.3$ for the Total PAHs, $\frac{11.5}{8.8} = 1.3$ for the Total - pyrene and $\frac{4.9}{4.3} = 1.1$ for the Total Carcinogenic PAHs. Thus, although the PAHs appear to be slightly more concentrated underground, the differences are small and may well be within experimental error of the analysis and sampling. Moreover, the limited number of above ground samples makes it even more difficult to conclude that there is any significant difference in the PAH concentrations in the two environments. Thus, it appears that the PAH levels are not significantly greater underground as was previously thought.

During the course of this work, two other experiments were carried out in an attempt to determine where the apparent increase in PAH concentration occurred. In one of these experiments, Hi Vol samples were collected simultaneously at the top and bottom of the

air intake shaft (Mine I) to see whether the PAH concentration changed as the air travelled down the shaft. The results in the first three columns of Table 8 show that the PAHs are present in a higher concentration at the bottom of the shaft. Although the Total PAH concentrations are higher at the bottom of the shaft, only eleven of the twenty-two individual analyses are higher and six of the twenty-two analyses are less concentrated at the bottom of the shaft. In fact, if one ignores the large increase in pyrene, the PAHs are not very much more concentrated at the bottom of the shaft. These small increases could easily account for the slightly higher PAH levels in the underground fresh air raises. Unfortunately, we are unable to provide a rationale for these results.

A second, similar experiment shows that the situation is not simple, however. The last two columns in Table 8 give the PAH concentrations found on Hi Vol filters collected simultaneously at the top and bottom of the air intake shaft on a cold day in the winter when the air was heated in a natural gas burner before it was pumped down the shaft. Since natural gas does not contain any PAHs, we had expected that the PAHs would not be increased when the air was heated. We were surprised to find, however, that the PAH concentrations were much lower at the bottom of the shaft. In fact, the Total PAHs, Total - pyrene and Total Carcinogenic PAHs at the bottom of the shaft only equalled 19.3%, 18.2% and 31.4% respectively, of the PAHs at the top of the shaft and in fact, all but one of the PAHs were at lower concentrations at the bottom of the shaft. The best explanation for this phenomenon is that some

TABLE 8 - The PAH concentrations at the top and the bottom of the air inlet shaft

	Concentrations in ng/m^3				
	Mine I Surface	1500' Level Mine I	1500' Level Mine I	Mine II Surface	Bottom of Intake Shaft Mine II
Pyrene	2.00	5.00	5.64	19.6	4.13
Fluoranthene	0.32	0.26	0.51	5.28	1.24
Benzo(a)anthracene*	0.52	0.70	2.20	3.82	0.75
Benzo(e)pyrene	0.84	0.57	0.50	12.4	0.41
Perylene	0.01	0.01	0.01	0.56	0.09
Benzo(k)fluoranthene	0.04	0.02	0.06	2.89	0.54
Benzo(a)pyrene*	0.02	0.02	0.01	1.31	0.29
Benzo(ghi)perylene*	0.09	0.18	0.15	2.13	0.83
Dibenzo(a,h)anthracene*	0	0	0	2.67	0
Dibenzo(def,mno)chrysene	0.01	0.01	0.01	0.30	0.06
Naptho(1234,def)chrysene*	0.17	0.05	0.57	1.83	1.77
Benzo(rst)pentaphene*	0.02	0.03	0.05	0.03	0.06
Total PAHs	4.04	6.82	9.69	52.8	10.2
Total-pyrene	2.04	1.84	4.05	33.2	6.04
Total Carcinogens	0.82	0.98	2.98	11.8	3.70
Sampling Time (Hr)	6.3	5.5	5.4	4.7	4.7

* Carcinogenic PAHs

of the PAHs in the air are burned as the air is heated in the furnace. This would reduce the quantities of PAHs in the air entering the mine and provide a better environment for the workers.

These experiments show that it is very difficult if not impossible, to know the PAH concentrations in the air entering a particular area of the mine. In fact, the location, the weather, the sampling time and whether the air entering the mine was heated, obviously affect the PAH level drastically and care will have to be taken in comparing results obtained on different days unless a background sample is taken during the test. Moreover, the sampling times should be shortened and/or standardized so that the losses of PAHs during sampling will be the same for each sample. Finally, some effort will have to be spent determining the real concentration of PAHs in the mine environment. This will presumably involve finding methods to trap the PAHs that pass through the Hi Vol filter.

The Influence of Blasting Agents:- One of the experiments carried out in 1980 had indicated that the PAH levels were higher after a blast. The actual experiment involved sampling the air entering and leaving a drift where a diesel was mucking and loading ore. During one of these tests, ore became jammed upstream from the Hi Vol sampling the air entering the drift and the miners loosened the ore by blasting it with approximately 400 pounds of Amex explosive. A comparison of the data in the first two columns of Table 9 shows that the concentrations of PAHs in the intake air on the day when the blast occurred, column 2, were significantly (five

TABLE 9 - PAH concentrations in the air after blasting operations using Amex and Watergel explosives

Concentrations in ng/m^3

	NICKEL MINE		NON-DIESELIZED MINE		NON-DIESELIZED MINE		
	Average Inlet Air	Intake Air + Amex 500' from blast	(Estimated) Amex 50'from blast	Amex 170' from blast	Watergel Corrected[a]	Amex Corrected[a,b]	Amex Fully Corrected[a,c]
Pyrene	10.3	51.8	1,156	904	746	96.2	289
Fluoranthene	1.0	4.4	39.3	22.0	16.9	655	1,965
Benzo(a)anthracene*	1.7	22.4	760	248	143	492	1,477
Benzo(e)pyrene	6.2	21.4	683	327	228	3,144	9,431
Perylene	0.1	0.2	2.4	1.7	4.5	47.1	141.2
Benzo(k)fluoranthene	0.7	1.9	15.2	13.6	11.2	28.5	85.6
Benzo(a)pyrene*	0.6	1.2	2.4	2.8	6.3	10.0	30.1
Benzo(ghi)perylene*	2.3	5.2	202	38.2	60.3	226	679
Dibenzo(a,h)anthracene*	-	-	137	63.9	0	74.6	224
Dibenzo(def,mno)chrysene	0.2	0.6	2.2	0.8	1.9	3.7	11.0
Naptho(1234,def)chrysene	0.4	7.6	51.0	24.1	20.5	87.1	261
Benzo(rst)pentaphene*	0.1	0.1	12.9	4.8	28.1	61.9	186
Total PAHs	23.6	116.8	3,063	1,651	1,267	4,926	14,780
Total - pyrene	13.3	65.0	1,907	747	521	4,830	14,490
Total carcinogens	5.1	36.5	1,165	382	258	952	2,857

a. Assumes no PAHs were collected between the time the Hi Vol sampler was started and the blast.

b. Assumes PAHs were collected for 55 minutes after the blast.

c. Assumes all the PAHs were collected in the first 16 minutes after the blast.

* Carcinogenic PAH

times) higher than the average PAH concentrations in the intake air on the other three days these tests were run (11). In fact, the PAH concentrations must have been extremely high in the air after the blast because the gases and particulate from the blast were present in the mine air for approximately 10% of the sampling period. This result had not been expected and was difficult to explain until we investigated the composition of the Amex explosive. This explosive contains six to seven percent diesel fuel or approximately 0.75 gallons of diesel fuel per 100 pounds of explosive. Thus, three gallons of diesel fuel was consumed in the blasting operation and we suggested that the PAHs were found in the air downstream from the blast because the PAHs in the diesel fuel (1, 21-23) were not burned in the explosion. This is reasonable because the PAHs are much higher boiling than the other components of diesel fuel and would therefore be harder to ignite and burn. As a result, they would be expelled into the atmosphere and would be collected on the Hi Vol sampler downstream from the blast.

Although this hypothesis was reasonable, it was possible that the high PAH concentrations were obtained because diesel particulate that had settled out on the walls and floors of the drift was blown into the air (picked up) as the shock wave from the blast passed down the drift and subsequently collected on the Hi Vol filter. If this were the case, the PAHs would not have been released during the blast with the Amex explosive. The results collected during the 1981-82 year prove conclusively that the Amex explosive was the source of the PAHs found after the blast.

The release of high concentrations of PAHs from the

explosives during the blasting operation has been confirmed by obtaining samples of the air after a small amount (70 pounds) of Amex explosive had been detonated in a non-dieselized mine. The blast was set off at the face of a development heading and PAH samples were collected approximately 50 and 170 feet from the blast site. There was no added ventilation in the drift and the blast gases were simply left to diffuse out of the drift. The sample collected 170 feet from the blast site at the exit to the drift was stopped after only 42 minutes (as soon as we could safely return to the drift). The filter was almost completely plugged at this time. Unfortunately, we could not get close enough to determine when the filter closest to the blast became completely plugged (the flow became zero). We did however, make educated guesses as to the shortest and the longest times that could have elapsed before the filter in the Hi Vol sampler became plugged and the flow through the filter ceased. When these times were used in calculating the volume of air sampled and subsequently the PAH concentrations, the maximum and minimum PAH concentrations varied by less than ten percent. The average PAH concentrations for the closer filter are given in column 3 of Table 9. The actual PAH concentrations found on the filter collected at the exit of the drift are given in column 4. In fact, the PAH concentrations 170 feet from the blast site are much higher than those in the background underground air (vide supra). For example, the Total PAHs, Total - pyrene and Total Carcinogenic PAHs in the air after the blast are 76, 65 and 78 times higher respectively, than the corresponding totals in the average air in the fresh air raises

underground in Sudbury. As expected, the PAH concentrations are even higher in the air closer to the blast site. The corresponding totals 50 feet from the blast site were 142, 166 and 238 times higher than totals for the average fresh air raise. In fact, the PAH concentrations found in this small blast were the highest that we had ever found in an underground mine. Even the total PAHs in the 170 foot sample were at least four times higher than the highest total PAHs found in any of the underground mine samples we have analyzed. It is worth noting however, that there was no ventilation used in the development heading where the blast occurred. This means that the PAH concentrations found in this experiment would probably exceed those found in a real mine where adequate ventilation was used.

The most important result of this experiment is that extremely high concentrations of PAHs were found when small amounts of Amex explosive were used in a non-dieselized mine. Obviously, since there had been no diesel activity in the mine, there could have been no diesel particulate (PAHs) on the walls or floors of the drift. This means that the PAHs collected on the Hi Vol filter could only have come from the Amex explosive. It is almost certain that the PAHs are an unburned residue of the PAHs that were in the diesel fuel that was used to make the Amex explosive.

These conclusions were confirmed by a second experiment that was done in the non-dieselized mine. In this experiment, a crosscut was being extended by 6 feet, Figure 2. The unique feature of this experiment was that the blast was done in two stages. In the first stage, the center of the drift was blown using

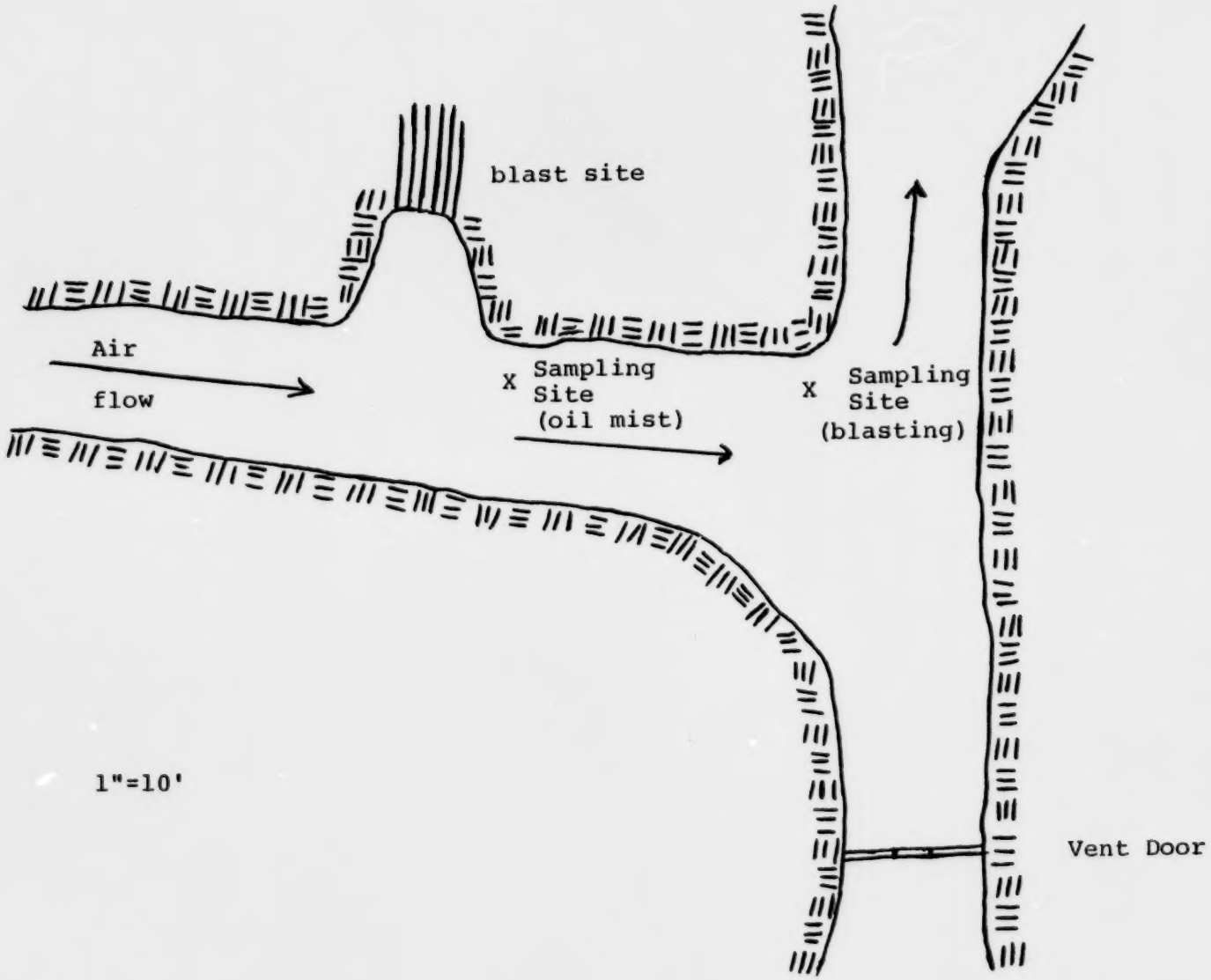


Figure 2. Level Plan for the non-dieselized mine blasting experiment.

approximately 35 pounds of a Watergel explosive that did not contain any diesel fuel. Once the center of the drift had been removed, the remaining holes were filled with a combination of 100 pounds of Amex (containing approximately seven pounds of diesel fuel) and approximately 15 pounds of the Watergel explosive.

The "corrected" PAH concentrations found approximately 40 feet from the blast sites, Figure 2, are given in columns 5, 6 and 7 of Table 9. The PAH concentrations quoted for these blasts were corrected by assuming that no PAHs were collected in the 6 minute period from the time the Hi Vols were started until the blast was set off. A comparison of the PAH levels in Sudbury air and those from the blast shows that this assumption was valid. The PAH sample was collected for 16 minutes after the blast. The PAH concentrations shown in column 5 of Table 9 were calculated using the volume of air sampled in 16 minutes. Since the air was clear when we re-entered the mine to shut off the Hi Vol, the PAHs were probably two or three times more concentrated while the blast gases and dust were present in the mine atmosphere. Unfortunately, we were not able to shut off the Hi Vol sampler 16 minutes after the Amex blast. In fact, the Amex PAH sample was collected for 55 minutes after the Amex had been detonated. As a result, the PAH concentrations in the air after the Amex explosion were calculated using two different sets of assumptions. First, the concentrations of the PAHs were calculated by i) assuming that no PAHs were collected in the period between starting the Hi Vol and detonating the blast, column 6, and ii) by assuming that all of the PAHs were collected in the first 16 minutes after the blast. This assumes

that it took the same length of time to clear the drift of PAHs whether the Amex or the Watergel explosive were used. The PAH concentrations calculated using the second set of assumptions are given in column 7. We believe that these concentrations are more accurate than those in column 6.

The data in columns 5 through 7 confirms that PAHs are released in the blasting operations. In fact, the Total PAHs, the Total - pyrene and the Total Carcinogenic PAHs are 59,45 and 53 times higher in the air after the Watergel blast than the corresponding totals for the average fresh air raise in Sudbury. The corresponding PAH levels in column 6 are 227,420 and 194 times higher than the totals for Sudbury air and the more realistic totals in column 7 are even larger, i.e., they are 684, 1260 and 583 times higher than the totals for the average fresh air raise. Again, since these samples were collected in a non-dieselized mine, the PAHs cannot be a result of diesel particulate that had been picked up from the walls or floors of the drift. Obviously, the PAHs must have been released in the blast.

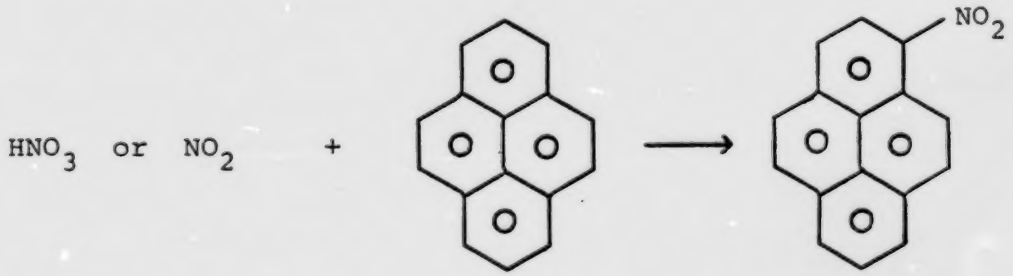
As expected, the air sampled after the blast with the diesel fuel based Amex explosive had much higher concentrations of PAHs than the air collected after the Watergel explosive had been detonated. In fact, the Total PAHs, Total - pyrene and Total Carcinogenic PAHs were 12, 28 and 11 times, respectively, more concentrated in the air collected after the Amex explosion. This result had been expected because it was believed that the PAHs in the blast gases were the unburned PAHs from the diesel fuel in the Amex explosive. The much higher PAHs in the blast gases from the Amex explosion are

certainly consistent with this hypothesis. Although we have not been able to ascertain the composition of the Watergel explosive, we do know that it does not contain any diesel fuel. As a result, we had expected much lower concentrations of PAHs from the Watergel explosion.

We were surprised however, to find that the PAH concentrations were so high when the Watergel explosive was used. Since no PAHs were expected from the explosive, we have attempted to identify other substances that could have produced the PAHs we observed. One possibility is that the PAHs in the blast gases are the unburned residue of the PAHs in the oil that was used to lubricate the jackleg drill during the drilling operation. If some of the drill oil had settle on the rock and was ignited during the blast, the low boiling hydrocarbons in the oil could burn leaving the high boiling PAHs behind in the same way the PAHs in the diesel fuel were left unburned in the Amex explosion. These PAHs would be blown into the mine air in the explosion and could be collected on the Hi Vol filter. Although this is possible, the amount of oil involved could not give all of the PAHs that were found in the air after the Watergel blast. We are unable to explain why large amounts of PAHs are found in the blast gases from the Watergel explosive.

The extremely high PAH concentrations in the mine air after an Amex explosion indicate that it is dangerous to work in air contaminated with the gases and dust from an explosion. Since many of the PAHs are carcinogens (mutagens) it was decided that the extract must be screened from a Hi Vol filter collected after an Amex blast with the Ames Salmonella bioassay test in order to learn whether

these substances were mutagenic. In fact, we had anticipated that the extract from such a sample might be highly mutagenic because recent work has suggested that most of the mutagenicity of diesel exhaust can be accounted for by the nitrated PAHs (nitro PAHs) that are in the diesel exhaust (24-27). These nitro PAHs are formed in a reaction between the PAHs and NO_2 or nitric acid that occurs in either the combustion chamber, the exhaust system or the catalytic purifier. A sample reaction is shown in equation 1.



[1]

If this reaction occurs at high temperatures in an engine or catalytic converter, it might occur at the high temperatures found in an Amex explosion because the PAHs are in the blast gases and both NO_3 and NO_2 are probably produced from the ammonium nitrate in the Amex explosive. The Hi Vol sample for Ames testing was collected approximately 80 feet from a blast using approximately 70 pounds of Amex explosive at the face of a 170 foot development heading in a non-dieselized mine. This ensured that there was no mutagenicity resulting from diesel exhaust particulate. Unfortunately, the exact volume of air sampled could not be determined because it was not possible to stop the Hi Vol before the filter became plugged with particulate and the flow rate through the filter was reduced to zero. However, the maximum and minimum volumes of air that could have been

sampled were estimated to be 30 and 28 m^3 respectively. Since these volumes were so close, a volume of 29 m^3 was used to calculate the mutagenicity of the sample. This would lead to an error of only three percent.

Although the specific mutagenicity and the maximum revertants per µg of extract are not unusually high, Table 10[1], the weight of the dichloromethane extract is extremely large. This means that the mine air is highly mutagenic. For example, the average revertants/m^3 of the mine air were 70,662 and 87,200 with and without S-9, respectively, and the maximum revertants/m^3 of mine air were 108,248 and 124,786 with and without S-9, respectively. Thus, the blast gases and particulate contain high concentrations of direct acting mutagens. In fact, this sample has by far the highest mutagenicity of any underground sample we have analyzed. For example, the most mutagenic sample of diesel exhaust had an average revertants/m^3 of 35,789. The average mutagenicity for all underground samples containing diesel exhaust is only 5,923 revertants/m^3. Finally, samples collected in the underground fresh air raises in Sudbury have an average of 48.5 revertants/m^3. Thus, the air from the blast is 1,800 times more mutagenic than the air in fresh air raises, 15 times more mutagenic than the average diesel exhaust contaminated air in underground mines and 2.4 times more mutagenic than the most mutagenic sample of diesel exhaust.

In conclusion, large concentrations of PAHs are released in the blasting operations in underground mines. The PAH concentrations in the air after a blast are particularly high when Amex explosive, which contains diesel fuel, is used. This is certainly consistent

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[1] Bioassay done by A.J. Horton, Ontario Research Foundation, Mississauga, Ontario.

TABLE 10 Ames mutagenicity of the dichloromethane extractables from a Hi Vol Filter collected after a blast with 70 lbs. of Amex explosive

Concentration Hi Vol Filter Extract /µg plate	S-9 mix +/-	Salmonella Tester Strains											
		TA-98 Histidine Revertants					(Average)	TA-100 Histidine Revertants					(Average)
1500	-	TOX						TOX					
1000	-	TOX						2678	2387				(2533)*
500	-	2128	1717				(1923)	2894	2711				(2803)
100	-	452	532				(492)	676	692				(684)
50	-	343	361				(352)	449	426				(438)
10	-	110	114				(112)	283	326				(305)
0	-	23	20	29	39	36	(29)	197	177	162	193	205	(187)
MUTAR		61.1						13.5					
1500	+	TOX						TOX					
1000	+	2138	1955				(2047)	TOX					
500	+	2333	2279				(2306)	2160	1860				(2010)
100	+	552	472				(512)	688	640				(664)
50	+	301	252				(277)	411	417				(414)
10	+	112	96				(104)	196	213				(205)
0	+	33	31	33	30	32	(32)	197	222	202	234	194	(210)
MUTAR		71.7						11.0					
Max Revertants/µg	-	8.3						11.8					
	+	7.2						4.5					
Specific Mutagenicity (Average Revertants/µg)	-	5.8											
	+	4.7											
Average Revertants/m^3	-	87,200											
	+	70,662											
Maximum Revertants/m^3	-	124,786											
	+	108,248											
Weight of Extract		436 mg											
Estimated Volume of air sampled		29 m^3											

with the hypothesis that the PAHs are an unburned residue of the PAHs in the diesel fuel. Finally, the extract from an Amex explosion is highly mutagenic in the Ames Salmonella bioassay.

The very high concentrations of PAHs released in blasting operations and the extremely high mutagenicity of the extract of the particulate collected after a blast, clearly indicate that miners should wait for some time before entering an area where blasting has occurred. This is particularly important when a diesel fuel based explosive has been used. Finally, these results suggest that it would be wise to determine the PAH concentrations and mutagenicity of the air after blasts by different explosives so that the safest explosive from an industrial health point of view could be found. This is particularly important because small amounts of explosives are often used to loosen muck piles and other blockages in the active working areas of the mine.

Oil Mists from Drilling Operations:- Diesels have been blamed for the presence of PAHs in the underground mine. It seemed probable however, that other substances might also add PAHs to the mine environment. One such substance proved to be the blasting agents that are used in almost every mine. Another possible source of PAHs was thought to be the oil mists that are produced in drilling operations. As a result, we collected air samples downstream from rock drilling operations to determine whether the oil mists produced in the drilling operation added PAHs to the mine air. We also collected a sample so that we could learn whether the oil mists were mutagenic. Two oil mist samples, one for PAH analysis and one for the Ames Salmonella

bioassay were collected in a non-dieselized "model" mine. This ensured that there was no other work going on in the mine which could generate PAHs and that there was no contamination by the PAHs in diesel exhaust. The drilling of a rock face in a short cross cut was done with a single jack-leg drill. Approximately one pint of oil was consumed in the drilling operation. The level plan and sampling site used in this experiment are shown in Figure 2.

The extracts from the two Hi Vol filters collected near the drilling operation contained a large amount of an oily material. This caused a problem because the PAH analysis and Ames test could not be done on this oily extract. This difficulty was overcome by removing the excess oils with a column chromatographic procedure that we had developed to remove the excess hydrocarbons from extracts from diesel fuels. The procedure was suitable because the PAHs could be recovered from the column quantitatively. The method involved dissolving the extract in 1 ml of cyclohexane and eluting the mixture from a 12 mm by 25 cm column of 60-200 mesh silica gel that had been partially deactivated with 15% water, with cyclohexane. The 30 to 100 ml fraction of the eluant contained the PAHs. After the cyclohexane had been removed from the 30 to 100 ml fraction, one of the residues (purified extracts) was analyzed for PAHs. The other purified extract was used in the Ames Salmonella bioassay.

The PAH concentrations in the air downstream from the drilling operations were quite high, Table 11. The Total PAHs are approximately 75% of the highest concentrations we have found in diesel exhaust samples underground. What is more important, however, is that the Total Carcinogenic PAHs are very high. For example, the highest Total

TABLE 11 - The PAH concentrations in the air downstream from a jack-leg drilling operation

	Concentration in ng/m^3
Pyrene	90.4
Fluoranthene	1.71
Benzo(a)anthracene*	112
Benzo(e)pyrene	112
Perylene	6.00
Benzo(k)fluoranthene	1.23
Benzo(a)pyrene*	0.31
Benzo(ghi)perylene*	8.85
Dibenzo(def,mno)chrysene	0.23
Naptho(1234,def)chrysene*	10.6
Benzo(rst)pentaphene*	0.72
Total PAHs	344
Total-pyrene	254
Total Carcinogens	133

* Carcinogenic PAH

Carcinogenic PAHs found in diesel exhaust samples was only 70.5 ng/m^3 or 53 percent of those found downstream from the drilling operation. The average Total Carcinogenic PAHs underground is approximately 30 ng/m^3. Thus, the air downstream from a single drill is high in carcinogenic PAHs, i.e., it is approximately 4.5 times higher than the average PAH levels underground. It is important to note that only one drill was used in this operation. Usually several drills operate at one time so that extremely high PAH levels must occur in the mine air.

Although the PAH concentrations are undoubtedly very high in drilling operations underground, it is still impossible to state whether the air is dangerous to the health of the miners. The problem in assessing the danger is that it is not known whether the oil mist (oil droplets) are respirable. Moreover, the PAHs would probably be dissolved in an oil droplet rather than on the surface of a diesel exhaust particle or in the vapour state. As a result, the PAHs may interact with the body in a totally different manner than the PAHs in diesel exhaust. We are obviously in no position to comment on the health effects of these oil mists.

The purified extract from one of these Hi Vol filters was analyzed with TA-98 and TA-100 Salmonella tester strains both with and without metabolic activation with S-9, Table 12[1]. In fact, the oil mist extract was negative with both tester strains both in the presence and absence of the metabolic activator, S-9. Although the oil mist contains large concentrations of PAHs the extracts as they were sampled and analyzed were non mutagenic. This may arise because the Ames tests are measuring the nitro PAHs that are present in

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[1] Bioassay done by A.J. Horton, Ontario Research Foundation, Mississauga, Ontario.

TABLE 12 Ames Salmonella test on the purified extract from a Hi Vol filter collected downstream from a jack-leg drilling operation

Concentration Hi Vol Filter Extract µl/ plate	S-9 mix +/-	Salmonella Tester Strains					
		TA-98			TA-100		
		Histidine Revertants[a]		(Average)	Histidine Revertants[a]		(Average)
0.5 µl	-	35	56	(46)	238	217	(228)
0.3 µl	-	46	37	(42)	217	249	(233)
0.1 µl	-	40	35	(38)	259	247	(253)
0.05 µl	-	25	47	(36)	254	267	(260)
0.03 µl	-	27	25	(26)	204	226	(215)
0.01 µl	-	28	34	(31)	220	249	(235)
Control 0	-			(23)			(244)
MUTAR[b]		1.0 Neg			0.06 Neg		
0.5 µl	+	129	55	(92)	224	242	(233)
0.3 µl	+	80	54	(67)	236	238	(237)
0.1 µl	+	51	58	(55)	228	238	(233)
0.05 µl	+	38	56	(47)	266	253	(260)
0.03 µl	+	45	53	(49)	205	200	(203)
0.01 µl	+	30	46	(38)	217	208	(213)
Control 0	+			(32)			(219)
MUTAR		1.8 Neg			0.18 Neg		

[a] 0.23289 g. of purified extract were dissolved in 20 ml DMSO.

[b] A Mutar of 2.5 is required for a positive Ames response.

diesel exhaust (24-27), and there are no nitro PAHs in the oil used in running the jack-leg drill. Although the PAHs are not mutagenic in this sample, they can be converted into more potent mutagens in the body (28,29). The very high concentrations of PAHs in the oil mists suggests that we should be very concerned about oil mists and attempt to find ways of reducing the PAHs released in the drilling operation.

The Effect of Mine Layout:- Some of the experiments carried out in the 1980-81 study suggested that mine layout played a significant role in determining the PAH concentrations in the mine air. For example, the PAH concentrations in the samples collected on one day in a salt mine were much higher than those found in the air in nickel mines. This was tentatively attributed to the larger drifts and lower air velocity found in the salt mine. The PAH levels in these samples also suggested that the PAHs travelled for large distances through the salt mine. The PAHs in nickel mines on the other hand, appear to settle out of the mine air very rapidly, i.e., in a short distance. We suggested that this very different behaviour was a result of differences in the ore (mine dust) and the humidity in the two mines. The salt particles that are in the air of a salt mine are highly ionic and should have little or no affinity for the carbonaceous diesel particulate. The less polar (less ionic) dust found in a nickel mine however, would have a higher affinity for the diesel soot. As a result, the diesel particulate would be absorbed onto or agglomerate with the mine dust in the nickel mine more readily. The heavier particles formed when the diesel particulate combined with

the mine dust could settle out onto the floor of the drift or could combine with water in the air to form still heavier particles that would fall to the floor of the drift. Although the higher humidity in the nickel mines could play a role in increasing the weight of the diesel particulate-mine dust particle, we do not believe the increased humidity plays an important role in the initial agglomeration because the carbonaceous diesel exhaust is hydrophobic and would not combine readily with a water droplet in the air.

During the 1981-82 contract year, we were able to collect samples in an uranium mine and in different salt and nickel mines. This was very useful because these samples confirmed that the hypotheses presented in the 1980-81 report were correct. In addition, these experiments indicated that other factors in the mine design also influence the PAH concentrations in the mine air.

A quick examination of the results obtained in the salt mine during the 1981-82 contract (salt mine II), Table 13, shows that the PAH concentrations are considerably higher underground than they are in the air entering the mine. In fact, the PAHs range from 329 times higher (Benzo(a)pyrene in the work site 2 sample) to a low of 2 times higher (Benzo(rst)pentaphene in the exhaust air 1 sample) than the PAHs in the air entering the mine. The Total PAHs range from 15 times higher (exhaust air 1 sample) to 106 times (work site 2 sample) (an average of 54 times) higher than the PAHs in the incoming air. The Total Carcinogenic PAHs show the same trend, i.e., they vary from a low of 16 times to a high of 78 times (an average of 36 times) the concentration of the carcinogenic PAHs in the incoming air. These levels are reminiscent of the very high PAH levels that were found in

Table 13 - Concentrations of the PAHs found in a salt mine, June 1981

	Concentration in ng/m^3				
	Work Site 1	Work Site 2	Exhaust Air 1	Exhaust Air 2	Intake Air
Pyrene	186	245	36.3	55.1	2.32
Fluoranthene	19.3	43.2	3.80	5.77	0.33
Benzo(a)anthracene*	14.9	10.8	8.28	11.3	0.45
Benzo(e)pyrene	55.8	54.7	2.80	16.1	0.31
Perylene	0.52	0.37	0.26	0.23	0.01
Benzo(k)fluoranthene	4.68	5.27	2.49	1.65	0.06
Benzo(a)pyrene*	1.08	2.30	1.67	1.04	0.01
Benzo(ghi)perylene*	5.33	6.06	3.75	2.19	0.24
Dibenzo(a,h)anthracene*	5.12	7.67	0.42	0.27	0
Dibenzo(def,mno)chrysene	0.65	0.44	0.49	0.22	0.01
Naptho(1234,def)chrysene*	4.49	42.5	0.62	2.43	0.16
Benzo(rst)pentaphene*	1.55	1.44	0.08	0.19	0.04
Total PAHs	299	420	61.0	79.1	3.94
Total-pyrene	113	175	24.7	24.0	1.62
Total Carcinogens	32.5	70.8	14.8	17.4	0.90
% CO_2	0.126[a]	0.126[a]	0.058[b]	0.058[b]	

a. The average CO_2 concentration during the time the two Work Site samples were collected.

b. The average CO_2 concentration during the time the two Exhaust Air samples were collected.

* Carcinogenic PAH

the salt mine tested in 1980 (salt mine I).

It is worth noting that the underground samples collected in salt mine II were all collected in less than three hours. The intake air sample at mine II on the other hand, was collected for 25.6 hours. Thus, some of the PAHs on the original sample would have been desorbed during the collection period and the PAH concentrations in the air entering the mine were undoubtedly much higher than those found by analyzing the filter, Table 13. In fact, if "corrected" Total PAHs were used (see pages 14-17), the Total PAHs underground at the exhaust air raise would only be an average of 6.2 times higher than the intake air and the PAHs at the work site would be an average of 28.2 times more concentrated than the air entering the mine. Since this same correction should be applied to the intake air sample collected at salt mine I, the PAH concentrations underground in the salt mines are not as high as we had thought.

Although the PAH levels in the salt mine are not as far above those of the intake air as we had suspected, they are still higher than those in other mines. In fact, when the PAH concentrations found in the same location in a mine are compared, the two salt mines have the highest PAH concentrations of all the mines we have tested.

The high PAH levels found in the salt mine have been attributed to the size of the drift (13). This relationship between PAH levels and drift size was expected because Canadian law requires a minimum of 100 cfm (2.83 m^3/min.) of ventilation per brake horsepower in all mining operations. Obviously, the velocity of the air in the drift will be inversely related to the cross-sectional area of the drift. Since removing the diesel emissions (PAHs) from a working

area would be more difficult when the air velocity in the drift is lower, one would expect to find higher PAH levels in mines with larger drifts. The results in Table 14 indicate that this relationship between the PAH concentrations and drift size does exist.

In order to make the comparison valid, we only selected samples that were collected in the same mining environment. For example, the samples were all collected between 100 and 300 feet downstream from a mucking operation. In addition, the Hi Vol samplers were situated so that the diesel passed within a few feet of the Hi Vol and the position of the sampler in the drift was the same in all of the experiments, i.e., it was positioned between 3 and 5 feet above the floor of the drift with the face of the filter parallel to the path of the diesel.

Plots of the Total PAHs, Total - pyrene, and the Total Carcinogenic PAHs in the drift against the cross-sectional area of the drift shows that a fairly high correlation exists between these two factors. In fact, the correlation coefficient for the plots are 0.78, 0.82 and 0.83, respectively. A typical plot is shown in Figure 3.

Although these correlation coefficients are not extremely high, they are surprisingly good when one considers all the factors that affect the results. For example, the PAH concentrations that are found in the air in some mines are very dependent on the distance between the Hi Vol sampler and the muck pile (vide infra) and although we have attempted to select similar samples, the distance varied. Moreover, different types of diesels burning different fuels were used in the four mines. This factor influences the PAH

Table 14 - Average PAH concentrations at similar environments in four different mine drifts.

PAH	Concentration in ng/m^3			
	Nickel Mine	Uranium Mine	Salt Mine I	Salt Mine II
Drift Size in sq.ft.	180	290	1000	1500
Pyrene	68.4	108	430	216
Fluoranthene	7.12	27.16	12.3	31.2
Benzo(a)anthracene*	19.9	11.49	4.48	12.9
Benzo(e)pyrene	7.92	20.0	25.4	55.3
Perylene	0.16	0.78	0.16	0.45
Benzo(k)fluoranthene	0.94	5.21	3.22	4.97
Benzo(a)pyrene*	0.39	3.75	0.42	1.69
Benzo(ghi)perylene*	1.48	9.11	6.60	5.69
Dibenzo(a,h)anthracene*	0	0	0	6.39
Dibenzo(def,mno)chrysene	0.20	0.38	0.88	0.55
Naptho(1234,def)chrysene*	2.28	4.50	12.1	23.5
Benzo(rst)pentaphene*	0.47	0.51	4.00	1.35
Total PAHs	109	191	499	360
Total-pyrene	40.5	82.9	69.6	144
Total Carcinogens	24.1	29.3	27.6	51.5
Number of samples averaged	4	2	2	2

* Carcinogenic PAH

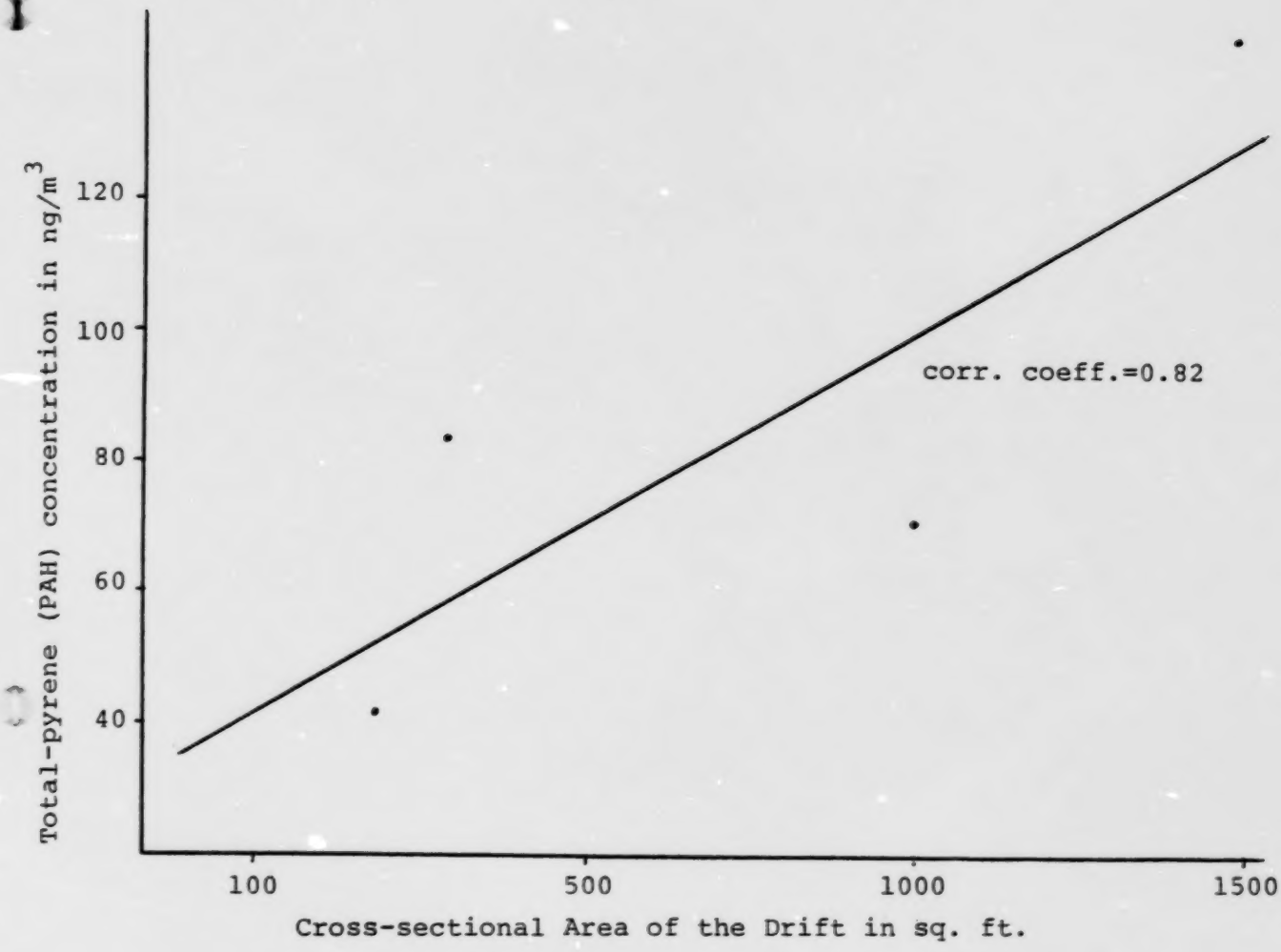

Figure 3. A typical PAH concentration versus drift size plot.

distribution and the Total PAHs markedly (vide infra). In light of these problems, the correlation coefficients for these plots are amazingly good and we believe that this relationship between drift size and PAH concentration does exist in dieselized mines. This means that there is a greater concern for the health of miners working in mines with large drifts. This in turn suggests that the ventilation requirements should be determined by the size of the drifts as well as by the horsepower of the diesel engine(s) used in

the mine. If this were done, larger volumes of air would be pushed through the larger drifts and a greater velocity of air in the drift would result. This would reduce the PAH levels in the mines with larger drifts and would mean that the miners would breathe clean (cleaner) air in all mines.

The results in Table 13 are interesting for other reasons. A comparison of the PAH concentrations from work site samples 1 and 2 shows that the PAH levels are significantly higher in sample 2 which was collected approximately 40 minutes after sample 1, i.e., the Total PAHs are 40% higher, the Total - pyrene is 54% higher and the Total Carcinogenic PAHs are 220 percent higher in sample 2. This greater level of contamination with diesel exhaust is confirmed by the concurrent increase in the NO_2 concentration from 2.5 to 3.0 ppm at a position 250 feet from the muck pile. Since the 1693 scoop was running constantly in the drift and three trucks were entering the drift on a 5 minute duty cycle during the time these samples were being collected, the PAH levels increase rapidly when the diesels are working in a particular development heading in the mine, Figure 4. The rapid increase in the PAH concentrations undoubtedly occurs because the auxiliary ventilation used in this development heading was not sufficient for the front end loader and the three diesel trucks.

In fact, the auxiliary ventilation of 15,000 cfm was far below, i.e., it was roughly 25% of the 100 cfm per brake horsepower required in the province of Ontario. This result shows that the PAH levels increase rapidly in a mine when the ventilation is inadequate.

The PAH concentrations for samples 1 and 2 at the exhaust air

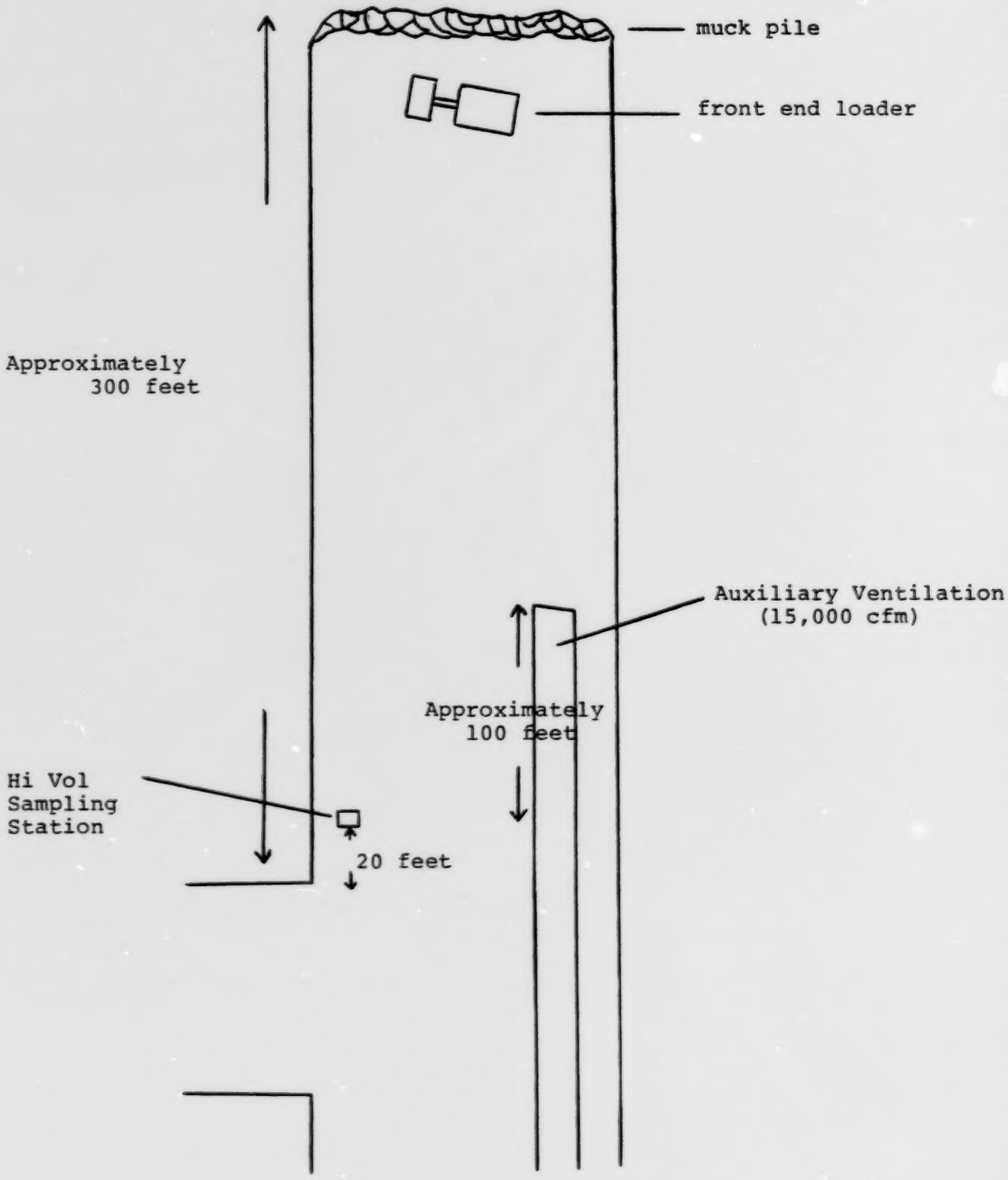

Figure 4. Level plan of the sampling site in salt mine II.

ramp vary in the same way. The Total PAHs are 58% higher, the Total - pyrene is 68% higher and the Total Carcinogenic PAHs are 17 % higher in sample 2 which was collected approximately 3 hours after sample 1. The higher levels found later in the day suggest that the PAH levels increase throughout the shift in a salt mine, i.e., that the PAHs are removed very slowly from the mine and are therefore higher when there has been more diesel traffic in the mine.

Although there was no firm experimental evidence to indicate that this also occurred in salt mine I, both the management and the miners believed that the PAH concentrations increased continually through the work week. Moreover, the observation that the PAH concentrations were higher at the exhaust air shaft than at the work site led us to conclude that the PAHs moved through the mine very slowly (14). Thus, it appears that the same behaviour was observed at both the salt mines tested. This suggests that this is a general feature of these mines. Again, increasing the ventilation in mines with larger drifts would probably eliminate this problem because the PAHs would be removed from the mine more quickly and would not become concentrated in the drifts.

The PAH concentrations at a work site and at an exhaust raise approximately two miles downstream from a work site in the two salt mines, Table 15, indicate that the design of the mine also influences the PAH concentrations in the air downstream from the diesel. The results in the first two columns of Table 15 show that seven of the eleven PAHs, as well as the Total - pyrene and Total Carcinogenic PAHs, are more concentrated at the exhaust air raise than they are at the work site in salt mine I. Thus, one must conclude that the particulate travels for large distances through this

Table 15 - The effect of mine design on the PAH concentrations in salt mines

	Concentration in ng/m^3			
	Average Salt Mine I at Diesel	Average Salt Mine I 2 miles from Diesel	Average Salt Mine II at Diesel	Average Salt Mine II 2 miles from Diesel
Pyrene	430	130	216	45.7
Fluoranthene	12.3	14.6	31.2	4.78
Benzo(a)anthracene*	4.48	40.4	12.9	9.78
Benzo(e)pyrene	25.4	38.8	55.3	9.45
Perylene	0.16	0.18	0.45	0.24
Benzo(k)fluoranthene	3.22	6.80	4.97	2.07
Benzo(a)pyrene*	0.42	0.58	1.69	1.36
Benzo(ghi)perylene*	6.60	11.3	5.69	2.97
Dibenzo(a,h)anthracene*	0	0	6.40	0.34
Dibenzo(def,mno)chrysene	0.88	0.18	0.55	0.35
Naptho(1234,def)chrysene*	12.1	5.82	23.5	1.52
Benzo(rst)pentaphene*	4.00	1.32	1.35	0.13
Total PAHs	499	250	360	78.7
Total-pyrene	69.6	120	144	33.0
Total Carcinogens	27.6	59.4	51.5	16.1

* Carcinogenic PAH

mine, i.e., the ratio of the (PAHs at the exhaust air raise / PAHs at the work site) vary from 0.51 for the Total PAHs to 1.7 to 2.2 for the Total - pyrene and the Total Carcinogenic PAHs, respectively. However, the Total PAHs, Total - pyrene and Total Carcinogenic PAHs at the exhaust air raise in salt mine II are much lower than the respective concentrations at the work site,i.e., the (PAHs at the exhaust air raise / PAHs at the work site) ratios for the Total PAHs, the Total - pyrene and Total Carcinogenic PAHs are all between 0.2 and 0.3. Obviously, the diesel particulate settles out much more quickly in mine II.

It is important to note that the samples were collected under almost identical conditions. For example, the distance between the two sampling sites, the type of ore, the humidity and the types of diesels were identical and the size of the drifts were similar, i.e., 25' x 40' in salt mine I and 30' x 50' in salt mine II. The only real difference between the two mines was the level plan. In salt mine I, the salt was deposited in a bed and a regular room and pillar method was used to mine the salt. In the second mine, the salt bed had been folded and the salt was mined in irregular drifts which followed the salt deposit. In the regular room and pillar mine (salt mine I) the air and the diesel particulate travelled around one corner in the two miles between the work site and the exhaust air raise. In salt mine II where the irregular drifts existed, the air changed directions 26 times in the two miles between the work site and the exhaust air raise.

Thus, although a significant portion (20-30%) of the diesel particulate was still in the air 2 miles downstream from the work

site in salt mine II, there is considerably less airborne particulate at the exhaust air raise in mine II than there is in mine I. This is particularly true when one realizes that the salt mine with the irregular drifts has the largest drifts (the lowest air velocity) and moreover, had some diesel activity in the area between the two sampling sites. In the room and pillar mine there was no diesel activity in the area between the sampling sites.

We believe the diesel particulate and thus, the PAHs settle out more quickly in the salt mine with irregular drifts because the particulate collides with the walls as the air and the particulate goes around corners on its way to the exhaust air raise. Since the particles could be absorbed on the walls or could loose momentum and settle out when they collide with the walls, the particulate should settle out more quickly than it would in a mine with straight drifts where collisions with the walls would be a minimum. This means that the mine environment is probably healthier in mines where the room and pillar method of mining is not used. This also means that less ventilation per brake horsepower would be required to maintain a healthy working environment in these mines.

Samples collected during the 1981-82 contract year in salt mine II, two nickel mines and an uranium mine have confirmed the results suggested by the 1980-81 study, i.e., that the PAHs travel for large distances in salt mines but settle out of the air very quickly (in short distances) in humid, hardrock mines. The different behaviour of the PAHs (diesel particulate) in the different mines is obvious when one examines the average PAH concentrations presented in Tables 15 and 16. The results in the first two columns of

Table 15 show that the PAH concentrations in salt mine I are generally higher 2 miles downstream from the work site than they are at the work site itself. In fact, seven of eleven of the individual PAHs are between 16 percent and nine times more concentrated at the exhaust air raise. In addition, the Total - pyrene and Total Carcinogenic PAHs are 1.7 and 2.2 times, respectively, more concentrated at the exhaust air raise.

The average PAH concentrations found in the air at the work site and two miles downstream at the exhaust air raise in salt mine II are presented in columns 3 and 4 of Table 15. Although the PAH concentrations are lower at the exhaust air raise than at the work site in this mine, the results indicate that the PAHs are carried for large distances in a salt mine. In fact, the Total PAHs, Total - pyrene and Total Carcinogenic PAHs 2 miles downstream from the work site still represent 22, 23 and 31% respectively, of the corresponding totals at the work site. Thus, significant amounts of PAHs are still found in the mine air at very large distances from the work site and one is forced to conclude that the PAHs can travel for several miles in a salt mine before they settle to the floor of the drift.

A completely different relationship between the PAH concentration and distance from the diesel exists in a nickel mine however. In nickel mine I, columns 1 and 2 of Table 16, the PAH concentrations in the air collected over a 4 hour period between 1000 and 2500 feet downstream from an area of high diesel activity were almost equal to those found in the fresh air entering the drift, i.e., the average Total PAHs, Total - pyrene and Total Carcinogenic PAHs in the fresh

TABLE 16 - PAH concentrations versus distance from the diesel

	Concentrations in ng/m^3					
	Average NICKEL MINE I		Average NICKEL MINE II		URANIUM MINE	
	at diesel	<2500' from diesel	at diesel	100' from diesel	Average 50' from muck pile	110' from muck pile
Pyrene	68.4	26.6	153	95.4	348	115
Fluoranthene	7.12	2.16	91.4	9.36	31.2	33.7
Benzo(a)anthracene*	19.9	3.09	10.1	7.02	34.4	18.5
Benzo(e)pyrene	7.92	1.92	19.0	10.0	52.8	22.4
Perylene	0.16	1.60	0.38	0.27	1.00	0.93
Benzo(k)fluoranthene	0.94	1.75	1.63	1.39	3.95	5.20
Benzo(a)pyrene*	0.39	1.02	1.60	0.89	2.65	3.50
Benzo(ghi)perylene*	1.48	2.52	3.06	1.10	8.30	7.30
Dibenzo(a,h)anthracene*	0	0.39	0	0	4.30	3.10
Dibenzo(def,mno)chrysene	0.20	0.21	0.38	0.12	0.43	0.34
Naptho(1234,def)chrysene*	2.28	1.79	3.89	2.63	8.35	2.40
Benzo(rst)pentaphene*	0.47	0.32	0.53	0.25	0.23	0.36
Total PAHs	109	41.1	285	128	496	212
Total-pyrene	40.5	14.5	132	33.0	148	97.7
Total Carcinogens	24.1	9.2	19.2	11.9	58.2	35.2

* Carcinogenic PAH

air raises (21.6, 11.5 and 4.9 ng/m^3, respectively) account for 53, 79 and 49% respectively, of the PAHs found in the drift. When the PAH levels in the air are examined in relationship to the amount of PAHs that were generated within 2500 feet of the sampling station, the PAH levels are very low. In fact, seven diesels totalling 1039 horsepower generated diesel exhaust for an average of three hours (three quarters of the sampling period), two jeeps and three drills were operated for short periods of time and 500 pounds of explosives were detonated during the sampling period. Since all of these operations generate PAHs (vide supra) one would expect very high concentrations of PAHs if the PAH laden particulate remained in the mine air for long periods of time (distances). The average Total PAHs, Total - pyrene and Total Carcinogenic PAHs found when samples are taken close to a single diesel in this nickel mine are 109, 40.5 and 24.1 ng/m^3 respectively and the PAHs in the air less than 2500 feet from all this activity, only equals 37% of the PAHs found near a single diesel engine. Thus, very low concentrations of PAHs remain in the air at reasonably short distances downstream from diesels in nickel mine I. This confirms that the PAHs settle out of the mine air very quickly in this mine.

The PAH concentrations found beside the diesel and approximately 100 feet away from the diesel in a stope in a different nickel mine (nickel mine II) confirm that the PAHs decrease rapidly with distance from the diesel in the nickel mines in and around Sudbury. For example, the data in columns 3 and 4 of Table 16[1], show that the

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[1] The raw data that was used to calculate these averages is given in Table 17.

average Total PAHs, Total - pyrene and Total Carcinogenic PAHs approximately 100 feet downstream from the diesel only account for 45, 25 and 62% respectively, of the corresponding totals obtained beside the diesel. The large decrease in the PAH concentrations that occurs in the very short distance (100 feet) clearly demonstrates that the PAHs do not remain in the mine air for large distances in nickel mines.

The results in column 5 and 6 of Table 16[1] are the PAH concentrations found in the mine air collected 50 feet and 110 feet from the muck pile in an uranium mine. Again, it is obvious that the PAH concentration decreases markedly in a short distance. The Total PAHs, Total - pyrene and Total Carcinogenic PAHs 110 feet from the muck pile are only 43, 66 and 60% respectively, of the corresponding totals 50 feet from the muck pile (15 to 20 feet behind the diesel during the mucking operation). Again, the PAH concentrations have decreased significantly in a very short distance. Thus, it would appear that the PAH levels decrease much faster with increasing distance from the diesel in humid, hardrock mines than they do in dry, salt mines. We suggest, (vide supra) that this difference is primarily, if not completely, a result of the greater affinity of the mine (ore) dust for the carbonaceous diesel particulate and PAHs in the hardrock mines. We do not know whether the humidity in these mines plays any role in the rapid settling of the PAHs. Whatever the mechanism of settling however, the PAHs settle out very rapidly in the humid, hardrock mines. This suggests that

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[1] The raw data that was used to calculate these averages is given in Table 17.

TABLE 17 - PAH concentrations in the air in a stope of nickel mine II and an uranium mine

	Concentrations in ng/m^3					
	NICKEL MINE II at diesel		NICKEL MINE II 100' from diesel		URANIUM MINE	
	Day 1	Day 2	Day 1	Day 2	50' from muck pile 1	50' from muck pile 2
Pyrene	151	156	64.5	126	305	392
Fluoranthene	8.37	9.90	12.1	6.64	35.7	26.7
Benzo(a)anthracene*	12.1	8.14	6.77	7.27	31.9	37.0
Benzo(e)pyrene	12.1	25.8	8.42	11.6	56.5	49.2
Perylene	0.47	0.27	0.33	0.21	0.69	1.29
Benzo(k)fluoranthene	2.29	0.96	1.80	0.98	1.42	6.55
Benzo(a)pyrene*	2.21	0.98	1.04	0.75	1.41	3.89
Benzo(ghi)perylene*	3.46	2.65	2.12	0.09	6.69	9.85
Dibenzo(a,h)anthracene*	0	0	0	0	4.15	4.44
Dibenzo(def,mno)chrysene	0.41	0.35	0.19	0.50	0.09	0.34
Naptho(1234,def)chrysene*	4.27	3.51	3.95	1.31	10.0	6.69
Benzo(rst)pentaphene*	0.52	0.53	0.35	0.16	0.46	0.01
Total PAHs	197	209	101	155	454	538
Total-pyrene	46.3	53.1	37.0	29.1	149	146
Total Carcinogens	22.6	15.8	14.2	9.57	54.6	61.9

* Carcinogenic PAH

only the operator of the diesel and those working close but down stream from the diesel, would be working in an atmosphere that contains concentrations of PAHs that are significantly higher than those working above ground. Since this reduces the number of miners that are exposed to high concentrations of PAHs (diesel particulate), the concern for the health of the miners in these mines is reduced. Unfortunately, this does not remove the concern for all miners in these mines.

The Mutagenicity of Diesel Exhaust Extracts

The Ames Salmonella bioassay (5,30,31) has been widely used to estimate the mutagenicity of diesel exhaust (16,33-37). A great deal of this work has been done in Canada (37) and some of these bioassays have been done in conjunction with PAH analyses of Hi Vol samples collected in dieselized underground mines (11,14). This work has provided information about the PAH levels and the mutagenicity of the extracts from Hi Vol samples collected in a fresh air raise and downstream from a Deutz diesel with i) no exhaust treatment devices, ii) a PTX catalytic converter or iii) a Dieseler III catalytic converter in the exhaust system of the vehicle. The results of these experiments showed that i) the exhaust from a Deutz engine with no exhaust treatment devices is 7 times more mutagenic[1] than the air in the fresh air raise, ii) that the exhaust was approximately 30% more mutagenic[1], i.e., the diesel exhaust was 9 times more mutagenic than the air in the fresh air raise, when a PTX catalytic converter was added to the exhaust system and

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[1] It is worth noting that these ratios were obtained whether the maximum revertants/m^3 or the average revertants/m^3 were used in calculating the mutagenicity of the diesel exhaust.

iii) that the exhaust was much more mutagenic when a Dieseler III catalytic converter was installed in the exhaust train of a Deutz diesel. In fact, the exhaust from the Dieseler III catalyst was 70 times more mutagenic[1] than the air in the fresh air raises, 11 times more mutagenic[1] than the exhaust from the diesel with no catalytic converter and 8.5 times more mutagenic[1] than the exhaust from a Deutz diesel with a PTX catalyst in the exhaust train.

The Ames testing (10,12) done in the 1980-81 study was extended in an effort to confirm some of the unexpected results obtained in the initial study and to extend our knowledge of the diesel exhaust problem in underground mines. All of the Ames Salmonella bioassays in this report were done at the Ontario Research Foundation in Mississauga, Ontario, under the supervision of Mr. A.J. Horton. The primary data supplied by Mr. Horton is presented in Tables 10, 12 and 18-27. All of these samples were collected on a teflon coated fiberglass (Pallflex) filter and extracted for 16 hours with dichloromethane in a soxhlet extractor. The extracts from the soxhlet were tested by a five strain bioassay with and without metabolic activation by the enzyme S-9. The details of this procedure are given in reference 11.

An examination of the data in Tables 18-27 shows that the extracts from the Hi Vol filters collected downstream from Deutz diesels fitted with a variety of different exhaust treatment devices are mainly comprised of direct acting mutagens, (they react in the absence of the enzyme S-9) and that there is little evidence of

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[1] It is worth noting that these ratios were obtained whether the maximum revertants/m^3 or the average revertants/m^3 were used in calculating the mutagenicity of the diesel exhaust.

TABLE 18: Ames Mutagenicity Plate Incorporation Assay Results for DCM Extractables for Sample 4, Table 28. (Deutz without Catalyst)

Concentration Filter Extract µg/Plate	S-9 mix +/-	Salmonella Tester Strains											
		TA-1537			TA-1538			TA-98			TA-100		
		Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)
800	-	61	58	(60)	120	160	(140)	206	202	(204)	367	337	(352)
400	-	56	38	(47)	121	125	(123)	127	141	(134)	265	263	(264)
200	-	45	41	(43)	93	94	(94)	82	106	(94)	244	271	(258)
100	-	22	16	(19)	86	76	(81)	43	58	(51)	213	225	(219)
80	-	17	8	(13	57	57	(57)	62	54	(58)	229	166	(197)
40	-	14	16	(15)	70	79	(75)	49	54	(52)	261	243	(252)
Control 0	-			(11)			(43)			(23)			(221)
Mutar		6.45			2.25			7.86			0.59		
800	+	87	59	(73)	153	154	(154)	264	245	(255)	391	386	(389)
400	+	78	57	(68)	137	128	(133)	185	188	(187)	293	366	(330)
200	+	48	47	(48)	104	100	(102)	135	128	(132)	252	275	(264)
100	+	30	27	(29)	81	97	(89)	88	91	(90)	211	229	(226)
80	+	33	24	(29)	80	74	(77)	71	82	(77)	189	194	(192)
40	+	22	22	(22)	85	55	(70)	55	53	(54)	186	185	(185)
Control 0	+			(10)			(40)			(28)			(211)
Mutar		7.3			2.85			8.1			0.84		
Max. Revertants/µg	-	0.16			0.8			0.72			0.7		
	+	0.55			0.75			0.65			0.29		

This bioassay was performed under the supervision of A.J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 19: Ames Mutagenicity Plate Incorporation Assay Results for DCM Extractables for Sample 5, Table 28. (Deutz without Catalyst)

Concentration Filter Extract µg/Plate	S-9 mix +/-	Salmonella Tester Strains											
		TA-1537			TA-1538			TA-98			TA-100		
		Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)
800	-	188	231	(210)	2365	2495	(2430)	2927	3715	(3321)	1080	1210	(1145)
400	-	211	177	(194)	3089	3834	(3462)	4158	3650	(3904)	618	801	(710)
200	-	154	113	(134)	1836	2246	(2044)	1955	2387	(2171)	490	518	(504)
100	-	103	90	(97)	988	1162	(1075)	1469	1588	(1529)	365	352	(359)
80	-	29	36	(33)	599	704	(652)	774	723	(749)	313	246	(280)
40	-	37	44	(41)	429	415	(422)	499	468	(484)	280	271	(276)
Control 0	-			(11)			(43)			(23)			(222)
Mutar		18.1			79.5			168.7			4.18		
800	+	242	249	(246)	3164	3542	(3353)	3866	3640	(3753)	796	659	(728)
400	+	276	776	(276)	3424	3013	(3219)	4428	4730	(4579)	521	653	(590)
200	+	162	173	(168)	2268	2862	(2565)	2905	3769	(3337)	457	419	(438)
100	+	82	73	(79)	972	961	(967)	1102	1372	(1251)	324	329	(327)
80	+	33	35	(34)	400	328	(364)	337	391	(364)	196	206	(201)
40	+	31	35	(33)	179	183	(181)	225	168	(197)	195	213	(204)
Control 0	+			(10)			(40)			(28)			(211)
Mutar		26.6			82.8			162.5			2.45		
Max. Revertants/µg	-	.86			16.3			15.1			1.41		
	+	.79			12.6			16.5			1.16		

This bioassay was performed under the supervision of A.J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 20: Ames Mutagenicity Plate Incorporation Assay Results for DCM Extractables for Sample 10, Table 28. (Dieseler III Catalyst)

Concentration Hi Volume Filter Extract µg/plate	S-9 mix +/-	Salmonella Tester Strains											
		TA-1537			TA-1538			TA-98			TA-100		
		Histidine Revertants		(Average)	Histidine Revertants		(Average)	Histidine Revertants		(Average)	Histidine Revertants		(Average)
400	-	725		(725)	9990	11253	(10622)	10260	10811	(10536)	1036	1018	(1027)
200	-	472	520	(496)	5648	7484	(6566)	8078	9957	(9018)	724	721	(723)
100	-	273	296	(285)	2786	2776	(2781)	4741	5119	(4930)	451	518	(485)
50	-	16	17	(17)	165	206	(186)	249	231	(240)	150	164	(157)
25	-	20	16	(18)	86	89	(88)	160	146	(153)	178	239	(209)
10	-	10	13	(12)	38	68	(53)	65	90	(80)	187	216	(202)
0	-	5 8 7 8 8		(7)	8 9 10 12 13		(10)	24 33 28 36 29		(30)	236 197 218 195 205		(210)
MUTAR		102.5			461.3			328.2			4.2		
400	+	761	677	(719)	11383	9677	(10530)	15735	14094	(14915)	625	534	(580)
200	+	383	377	(380)	4676	4882	(4779)	6642	7768	(7205)	382	344	(363)
100	+	181	171	(176)	1630	1503	(1567)	2808	2722	(2765)	272	317	(295)
50	+	13	22	(18)	71	89	(80)	102	112	(107)	191	168	(180)
25	+	17	18	(18)	44	43	(44)	62	66	(64)	157	155	(156)
10	+	8	13	(11)	18	26	(22)	48	29	(39)	171	187	(179)
0	+	13 4 7 9 13		(9)	11 17 20 20 13		(16)	24 39 34 26 41		(33)	225 221 168 209 229		(210)
MUTAR		101.4			618.5			465			2.3		
Max Revertants/µg	-	2.9			32.8			49.0			2.8		
	+	1.9			26.3			37.2			0.9		

S-9 - Metabolic Activation Mixture

This bioassay was performed under the supervision of A.J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 21: Ames Mutagenicity Plate Incorporation Assay Results for DCM Extractables for Sample 11, Table 28. (Dieseler III Catalyst)

Concentration Hi Volume Filter Extract µg/plate	S-9 mix +/-	Salmonella Tester Strains											
		TA-1537			TA-1538			TA-98			TA-100		
		Histidine Revertants		(Average)	Histidine Revertants		(Average)	Histidine Revertants		(Average)	Histidine Revertants		(Average)
304	-	350	314	(332)	5432	5162	(5297)	6901	5994	(6448)	756	669	(713)
152	-	232	211	(222)	2819	2722	(2771)	4525	5000	(4763)	574	570	(572)
76	-	163	169	(166)	890	1112	(1001)	1912	2505	(2209)	372	362	(367)
38	-	27	30	(29)	253	238	(246)	390	369	(380)	184	171	(178)
19	-	18	27	(23)	128	123	(126)	230	184	(207)	168	236	(202)
7.6	-	12	13	(13)	51	65	(58)	101	103	(102)	208	179	(194)
0	-			(7)			(10)			(30)			(210)
MUTAR		46.4			229.9			207			2.6		
304	+	291	296	(294)	5259	5389	(5324)	7387	6372	(6880)	406	418	(412)
152	+	170	195	(183)	2700	2311	(2506)	4093	4417	(4255)	350	331	(341)
76	+	102	126	(114)	709	729	(719)	1912	2106	(2009)	236	255	(246)
38	+	20	22	(21)	97	117	(107)	145	165	(155)	150	153	(152)
19	+	20	22	(21)	51	55	(53)	91	82	(87)	146	208	(177)
7.6	+	12	10	(11)	40	29	(35)	49	50	(50)	164	171	(168)
0	+			(9)			(16)			(33)			(210)
MUTAR		40.7			321.2			214.3			1.2		
Max Revertants/µg		2.0 1.4			18.2 17.5			31.1 27.8			2.4 0.9		

S-9 - Metabolic Activation Mixture

This bioassay was performed under the supervision of A.J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 22: Ames Mutagenicity Plate Incorporation Assay Results for DCM Extractables for Sample 12, Table 28. (Dieseler III Catalyst)

Concentration Hi Volume Filter Extract µg/plate	S-9 mix +/-	Salmonella Tester Strains			
		TA-1537 Histidine Revertants (Average)	TA-1538 Histidine Revertants (Average)	TA-98 Histidine Revertants (Average)	TA-100 Histidine Revertants (Average)
500	-	2959	24500 24600 (24550)	35000 29300 (32150)	3553 3348 (3451)
400	-	2754	23800 19100 (21450)	38700 29000 (33850)	2765 3121 (2943)
300	-	3132	16600 13700 (15500)	39000 37000 (38000)	2581 2495 (2538)
200	-	1674	12700 11600 (12150)	21800 16300 (19050)	1955 2117 (2036)
100	-	931	5904 6714 (6309)	17200 9594 (13397)	1064 1102 (1083)
50	-	425	4302 3366 (3834)	6930 6100 (6515)	625 652 (639)
0	-	6 7 9 10 3 (7)	12 13 13 15 16 (14)	23 20 29 39 36 (29)	197 177 162 193 205 (187)
MUTAR		446.4	1066.7	1224.8	16.8
500	+	2657	31600 31800 (31700)	44700 39400 (42050)	2128 2030 (2079)
400	+	3197	21100 19000 (20050)	36400 41900 (39150)	1922 2084 (2003)
300	+	2646	20700 23500 (22100)	33000 29500 (31250)	1825 2117 (1971)
200	+	1447	12000 10100 (11050)	22500 24000 (23250)	1168 1138 (1153)
100	+	661	5962 4579 (5271)	10800 10000 (10400)	566 652 (609)
50	+	302	1512 1814 (1662)	2754 3769 (3262)	406 416 (411)
0	+	14 7 5 9 12 (9)	20 16 15 19 16 (17)	33 31 33 30 32 (32)	197 222 202 234 194 (210)
MUTAR		455.4	1863.7	1313	11.4
Max Revertants/µg	-	10.4	76.4	134	9.2
	+	8.8	73.6	116	5.9

TA-1537 was run at one plate per conc. because of sample limitations

S-9 = Metabolic Activation Mixture

This bioassay was performed under the supervision of A. J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 23: Ames Mutagenicity Plate Incorporation Assay Results obtained with Nitroreductase deficient strains for DCM Extractables for Sample 13, Table 28. (Dieseler III Catalyst)

Concentration Filter Extract µg/Plate	S-9 mix +/-	Salmonella Tester Strains								
		TA-98			TA-98 NR			TA-98 1.8 DNP6			TA-98 NR/BR		
		Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)
1000	-	42894	77112	(60003)	11574	10764	(11169)	309	383	(346)	70	47	(59)
500	-	41238	47115	(44176)	7974	7866	(7920)	171	221	(196)	55	67	(61)
200	-	22320	25794	(24057)	3229	3402	(3315)	107	110	(108)	28	32	(30)
100	-	9360	7092	(8226)	2203	1436	(1819)	48	57	(53)	14	20	(17)
80	-	6048	6766	(6407)	1987	1577	(1782)	25	51	(38)	17	13	(15)
40	-	3942	3888	(3915)	846	853	(850)	30	32	(31)	21	12	(17)
20	-	2851	3150	(3000)	478	493	(486)	34	36	(35)	13	23	(18)
Control 1	-			(34.2)			(14.6)			(17.7)			(15)
Mutar		1764			744			19.3			2.9		
1000	+	50220	55188	(52704)	8694	8028	(8361)	382	329	(355)	58	51	(54)
500	+	29106	30131	(29618)	3834	3834	(3834)	172	100	(136)	31	32	(32)
200	+	4644	4284	(4464)	623	522	(572)	55	49	(52)	20	12	(16)
100	+	1750	1415	(1582)	176	212	(194)	61	50	(55)	34	21	(28)
80	+	523	538	(530)	138	155	(146)	32	32	(32)	18	23	(20)
40	+	246	263	(254)	75	88	(81)	31	35	(33)	23	22	(23)
20	+	155	170	(162)	44	48	(46)	40	44	(42)	15	23	(19)
Control 0	+			(47.4)			(26.2)			(35.4)			(26)
Mutar		1120			326			9.1			1.0		
Max. Revertants/µg	-	148.3			23.5			0.9			0.2		
	+	59			8.3			0.4			0.02		

TABLE 24: Ames Mutagenicity Plate Incorporation Assay Results for Sample 14, Table 28.

Concentration Filter Extract (µg/P)	S-9 mix +/-	Salmonella Tester Strains									
		TA-1535		TA-1537		TA-1538		TA-98		TA-100	
		Histidine Revertants	(Average)	Histidine Revertants	(Average)	Histidine Revertants	(Average)	Histidine Revertants	(Average)	Histidine Revertants	(Average)
165	-	26 17	(22)	63 40	(52)	194 166	(180)	272 401	(337)	Toxicity	(T)
82.5	-	31 18	(25)	38 43	(41)	135 129	(132)	308 293	(301)	412 439	(426)
33	-	13 21	(17)	30 28	(29)	96 96	(96)	162 159	(161)	287 250	(269)
16.5	-	19 23	(21)	10 9	(10)	33 25	(29)	44 53	(49)	253 246	(250)
8.25	-	23 21	(22)	4 4	(4)	24 16	(20)	47 39	(43)	243 241	(242)
3.3	-	19 28	(24)	8 5	(7)	29 20	(25)	35 37	(36)	251 213	(232)
Control 0	-		(18)		(6)		(15)		(29)		(194)
MUTAR		0.35		6.57		8.68		10.27		1.20	
165	+	13 18	(16)	27 25	(26)	190 86	(138)	226 162	(194)	248 262	(255)
82.5	+	15 15	(15)	43 32	(38)	69 96	(69)	191 152	(172)	236 216	(226)
33	+	22 20	(21)	14 22	(18)	37 58	(48)	91 94	(93)	198 186	(192)
16.5	+	16 18	(17)	14 9	(12)	35 34	(35)	50 60	(55)	149 153	(150)
8.25	+	10 13	(12)	5 6	(6)	29 29	(29)	31 47	(39)	152 139	(146)
3.3	+	19 17	(18)	7 9	(8)	18 26	(22)	18 27	(23)	165 163	(164)
Control 0	+		(13)		(6)		(15)		(26)		(158)
MUTAR		0.62		2.86		7.69		5.79		0.60	
Max Revertants/µg	-	1.82		0.70		3.03		4.42		11.52	
	+	1.51		0.61		2.12		2.03		1.03	

S-9 = Metabolic Activation Mixture TOX = Killing of the Salmonella tester strains by the sample material

This bioassay was performed under the supervision of A.J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 25: Ames Mutagenicity Plate Incorporation Assay Results for Sample 15, Table 28.

Concentration Filter Extract (µg/P)	S-9 mix +/-	Salmonella Tester Strain									
		TA-1535		TA-1537		TA-1538		TA-98		TA-100	
		Histidine Revertants	(Average)	Histidine Revertants	(Average)	Histidine Revertants	(Average)	Histidine Revertants	(Average)	Histidine Revertants	(Average)
200	-	10 15	(13)	37 26	(32)	131 212	(172)	191 142	(167)	350 282	(316)
100	-	18 25	(22)	30 27	(29)	103 95	(99)	123 156	(140)	279 292	(286)
40	-	16 16	(16)	11 18	(15)	52 34	(43)	75 90	(83)	224 186	(205)
20	-	19 18	(19)	7 11	(9)	33 20	(27)	29 45	(37)	200 199	(200)
10	-	24 20	(22)	7 8	(8)	25 23	(24)	33 55	(44)	236 179	(208)
4	-	18 12	(15)	8 11	(10)	19 23	(21)	30 34	(32)	190 207	(199)
Control 0	-		(18)		(6)		(15)		(29)		(194)
MUTAR		0.20		3.70		8.26		4.60		0.63	
200	+	Toxicity	(T)	Toxicity	(T)	Toxicity	(T)	164 140	(152)	250 260	(255)
100	+	Toxicity	(T)	Toxicity	(T)	Toxicity	(T)	100 98	(99)	197 200	(199)
40	+	27 34	(25)	14 19	(17)	48 30	(39)	56 46	(51)	155 200	(178)
20	+	10 9	(10)	11 3	(7)	14 16	(15)	38 42	(40)	155 179	(167)
10	+	14 16	(15)	6 3	(5)	28 14	(21)	42 30	(36)	157 175	(166)
4	+	11 13	(12)	5 10	(8)	23 25	(24)	45 34	(40)	138 170	(154)
Control 0	+		(13)		(6)		(15)		(26)		(158)
MUTAR		0.92		1.57		1.50		4.34		0.60	
Max Revertants/µg	-	0.40		1.0		1.5		1.5		1.4	
	+	0.30		0.50		2.25		3.5		0.80	

S-9 = Metabolic Activation Mixture TOX = Killing of the Salmonella tester strains by the sample material

This bioassay was performed under the supervision of A.J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 26: Ames Mutagenicity Plate Incorporation Assay Results for DCM Extractables for Sample 16, Table 28. (Detroit Diesel without Catalyst)

Concentration Filter Extract µg/Plate	S-9 mix +/-	Salmonella Tester Strains											
		TA-1537			TA-1538			TA-98			TA-100		
		Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)
800	-	10	5	(8)	25	19	(22)	44	41	(43)	265	236	(251)
400	-	14	10	(12)	20	24	(22)	48	48	(48)	260	298	(279)
200	-	14	6	(10)	10	16	(13)	39	41	(40)	256	271	(264)
100	-	9	7	(8)	20	21	(21)	32	38	(35)	241	297	(269)
80	-	7	12	(10)	11	11	(11)	29	21	(25)	230	204	(217)
40	-	8	14	(11)	16	14	(15)	33	32	(33)	240	291	(266)
Control 0	-			(7)			(14)			(27)			(235)
Mutar		0.6			0.6			0.8			0.2		
800	+	15	16	(16)	43	33	(38)	46	43	(45)	287	304	(296)
400	+	10	13	(13)	25	21	(23)	43	45	(44)	225	190	(268)
200	+	9	28	(19)	40	22	(31)	55	42	(49)	222	295	(259)
100	+	20	11	(17)	17	22	(20)	38	49	(44)	275	258	(267)
80	+	7	16	(12)	20	16	(18)	34	32	(33)	294	289	(292)
40	+	15	6	(11)	17	20	(19)	31	33	(32)	287	304	(296)
Control 0	+			(8)			(19)			(32)			(225)
Mutar		1.4			1.0			0.5			0.3		
Max. Revertants/µg	-												
	+												

This bioassay was preformed under the supervision of A. J. Horton, Ontario Research Foundation, Mississauga, Ont.

TABLE 27: Ames Mutagenicity Plate Incorporation Assay Results for DCM Extractables for Sample 17, Table 28. (Detroit Diesel without Catalyst)

Concentration Filter Extract µg/Plate	S-9 mix +/-	Salmonella Tester Strains											
		TA-1537			TA-1538			TA-98			TA-100		
		Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)	Histidine Revertants		(average)
800	-	11	13	(12)	20	20	(20)	35	30	(33)	311	354	(333)
400	-	9	10	(10)	16	21	(19)	33	24	(29)	288	378	(333)
200	-	13	14	(14)	17	15	(16)	31	34	(33)	287	254	(271)
100	-	20	14	(17)	24	16	(20)	34	36	(35)	224	249	(237)
80	-	6	9	(8)	12	19	(16)	20	23	(22)	212	223	(218)
40	-	8	11	(10)	17	17	(17)	31	25	(28)	267	256	(262)
Control 0				(7)			(14)			(27)			(235)
Mutar		1.4			0.4			0.3			0.4		
800	+	26	14	(20)	35	47	(41)	64	67	(66)	259	290	(275)
400	+	24	22	(23)	36	26	(31)	47	46	(47)	234	239	(237)
200	+	23	34	(29)	18	23	(20)	57	48	(53)	266	291	(279)
100	+	26	29	(28)	9	25	(17)	40	32	(36)	284	276	(280)
80	+	8	10	(9)	17	12	(15)	22	27	(25)	242	272	(257)
40	+	10	10	(10)	19	14	(17)	31	29	(30)	240	257	(249)
Control 0				(8)			(19)			(32)			(225)
Mutar		2.6			1.2			1.1			0.2		
Max. Revertants/µg	- +												

This bioassay was performed under the supervision of A.J. Horton, Ontario Research Foundation, Mississauga, Ont.

promutagens (compounds that are converted into direct acting mutagens by the enzyme S-9) in the extracts. The high mutagenicity observed with TA-1538 and TA-1537 strains and the low mutagenicity with TA-100 indicate that the mutagenic response is primarily of the frame shift mutation type, i.e., the mutagens act by disrupting the DNA replication. The small, finite response to TA-100 suggests that the extracts may contain a small amount of base pair mutagens (compounds that are incorporated into the DNA molecules thus changing their chemical reactions).

The data in Table 23 is interesting because it demonstrates how the extract from a filter collected downstream from a Deutz diesel with a Dieseler III catalytic converter responds to Salmonella strains TA-98NR, a strain that does not react with mono nitro PAHs and TA-98-1,8-DNP6 which does not react with dinitro PAHs and TA-98NR/BR which does not react with any nitro PAHs. The much lower response with the TA-98NR strain indicates that a significant portion of the mutagenic response provided by TA-98-S9 is due to mono nitro compounds. The even lower response with TA-98-1,8-DNP6-S9 indicates that even greater amounts of dinitro PAHs are present in the extract from the exhaust from the Dieseler III catalyst. Finally, the mutar of 2.9 without S-9 and 1.0 with S-9 for the TA-98NR/BR strain indicates that all or almost all of the mutagenic activity is due to nitrated PAHs. It is worth noting that this conclusion has also been suggested by other researchers working with different types of diesels (24-27). In particular, Horton (38) has found that the nitro PAHs account for all of the mutagenic activity in the extracts from filters collected downstream from a bare Deutz engine.

Thus, it appears that the Ames Salmonella bioassay is providing a measure of the nitro PAHs in diesel exhaust samples.

The results of the Ames Salmonella bioassay with strain TA-98 in the absense of S-9 on the samples collected underground between 1980 and 1982 are presented in Table 28. The mutagenicity is expressed in three different ways, i.e., as the specific mutagenicity (the average revertants/µg of extract) and as the maximum and average revertants/m^3 of air sampled. The latter two values were obtained by multiplying the maximum revertants/µg of extract and the specific mutagenicity respectively, by the weight of the extract and dividing by the volume of mine air that had passed through the Hi Vol sampler. Table 28 gives all of these results as well as the Total PAHs, the Total - pyrene and the Total Carcinogenic PAHs, the percent CO_2 and the NO_2 levels found at each sampling site.

Sample 1 in Table 28 gives the mutagenicity and PAH concentrations obtained for a combined intake air sample. Two intake air samples were combined because one sample did not give enough extract for a five strain Ames bioassay. This sample is important because it gives the background mutagenicity of the air in the fresh air raises underground.

The next set of samples give the mutagenicity of the exhaust collected downstream from a Deutz diesel that did not have any exhaust treatment devices. Two of these samples (2 and 3) were collected during the 1980-81 contract year. Unfortunately, the mutagenicity of these two samples was very different. For example, the extract from sample 2 had a specific mutagenicity of 0.35, a maximum revertants/m^3 of 191 and an average revertants/m^3 of 26.8. The corresponding values

Table 28 - The mutagenicity and PAH concentrations in dieselized underground mines.*

Sample	Specific Mutagenicity TA-98-S9	mg Extract	Vol. Air m^3	Max. rev/m^3 TA-98-S9	Average Rev. / m^3 TA-98-S9	Total PAHs ng/m^3	Total-Pyrene ng/m^3	Total Carcinogenic PAHs ng/m^3	% CO_2	NO_2 ppm
1. Intake Air (1981)	0.85	42.6	746.9	83.8	48.5	67.2[e]	21.7[e]	5.97[e]	NM	NM
Average Intake Air(1980-82)						21.6	11.5	4.9		
2. Deutz No Catalyst (1981)	0.35	17.1	223.6	191	26.8	30.7[f]	18.3	7.31	0.105	0.66
3. Deutz No Catalyst (1981)	5.6	40.8	360.8	916	633	26.4[f]	15.7	5.76	0.081	0.98
4. Deutz No Catalyst	0.39	50.2	108.3	334	181	NM	NM	NM	NM	NM
5. Deutz No Catalyst	11.2	41.8	129.3	4,882	3,621	NM	NM	NM	NM	NM
Average Deutz No Catalyst	(2.1)[a] 4.4[b]			(480)[a] 1581[b]	(280)[a] 1115[b]	28.6	17.0	6.54		
6. Deutz + PTX Catalyst (1981)	2.7	69.0	464.9	654	401	32.4[g]	20.5	13.3	0.066	NM
7. Deutz + PTX Catalyst (1981)	4.0	54.3	411.2	727	528	32.4[g]	20.5	13.3	0.066	NM
Average Deutz + Catalyst	3.4			691	465	32.4	20.5	13.3		
8. Deutz + Dieseler III Catalyst (1981)	45.7	37.2	444.2	5,611	3,827	27.4[f]	11.1	3.43	0.085	0.86
9. Deutz + Dieseler III Catalyst (1981)	88.3	14.9	400.0	6,184	3,289	26.3[f]	5.73	1.87	0.062	0.82
10. Deutz + Dieseler III Catalyst	47.0	20.9	129.3	7,939	7,597	106[h]	48.2	33.1	0.105	0.30
11. Deutz + Dieseler III Catalyst	27.0	11.4	116.3	3,056	2,647	65.9[h]	35.2	19.4	0.105	0.30
12. Deutz + Dieseler III Catalyst	121	23.4	117.2	26,800	24,219	111[i]	34.8	29.5	NM	NM

Table 28 (Cont'd)

	Sample	Specific Mutagenicity TA-98-S9	mg Extract	Vol. Air m^3	Max. rev/m^3 TA-98-S9	Average Rev. / m^3 TA-98-S9	Total PAHs ng/m^3	Total-Pyrene ng/m^3	Total Carcinogenic PAHs ng/m^3	% CO_2	NO_2 ppm
13.	Deutz + Dieseler III Catalyst	103	54.9	158.0	51,530	35,789	154[i]	45.4	16.2	NM	NM
	Average Deutz + Dieseler III Catalyst	72			(5698)[c] 16,854[d]	(4340)[c] 12,895[d]	81.8	30.1	17.2		
14.	Caterpillar + PTX Catalyst + High NO_2	3.65	6.6	19.08	1,528	1,263	299[j]	113	32.5	0.126	3.0
15.	Caterpillar + PTX Catalyst + High NO_2	1.32	8.0	12.59	953	839	420	175	70.8	0.126	4.0
	Average Caterpillar + PTX Catalyst + High NO_2	2.49			1,241	1,051	360	144	51.6		
16.	Detroit Diesel No Catalyst	0	30.72	16.1	0	0	496[k]	148	58.3	0.151	0.7
17.	Detroit Diesel No Catalyst	0	26.6	17.5	0	0	212[l]	97.7	35.2	0.134	0.7
	Average Detroit Diesel No Catalyst				0	0	354	123	46.8		
18.	Oil Mist	0	232.9	272.8	0	0	344[m]	254	133	NM	NM
19.	Blasting	7.38	436	28.95	120,828	111,146	2,357[n]	1,327	773	NM	NM

a. Average for samples 2-4.

b. Average for samples 2-5.

c. Average for samples 8-11.

d. Average for samples 8-13.

e. These values are the average of 2 intake air samples (column 5, Table 9 (1981 report) and Table 29 (this report)) collected beside the samples used in the Ames analysis. The PAH concentrations in these samples were unusually high. The average PAH concentrations in the fresh air raises over a two year period are given for comparison.

f. Table 9, 1981 final report.

g. Table 5, 1981 final Report

h. Table 1, this report.

i. Table 29, this report.

j. Table 13, this report.

k. Table 17, an average of columns 5 and 6, this report.

l. Table 16, this report.

m. Table 11, this report.

n. Table 9, an average of columns 3 and 4, this report.

NM - not measured.

* The PAH analyses and the Ames bioassay were done on different samples collected on the same day at the same site in the mine.

TABLE 29 - The individual PAH concentrations for some of the Hi Vol samples in Table 28

	Concentrations in ng/m^3		
	Intake Air 1981	Deutz+Dieseler III Catalyst-Sample 12	Deutz+Dieseler III Catalyst-Sample 13
Pyrene	54.3	76.5	109
Fluoranthene	1.22	3.80	11.4
Benzo(a)anthracene*	0.41	25.3	10.9
Benzo(e)pyrene	19.3	0.28	16.2
Perylene	0.10	0.13	0.21
Benzo(k)fluoranthene	0.67	0.86	1.21
Benzo(a)pyrene*	0.38	0.29	0.34
Benzo(ghi)perylene*	0.80	1.48	1.92
Dibenzo(a,h)anthracene*	0	0	0
Dibenzo(def,mno)chrysene	0.10	0.22	0.20
Naptho(1234,def)chrysene*	2.76	1.91	2.58
Benzo(rst)pentaphene*	0.44	0.53	0.44
Total PAHs	80.5	111	154
Total-pyrene	26.2	34.8	45.4
Total Carcinogens	4.79	29.5	16.1

* Carcinogenic PAH

for sample 3 were 5.6, 916 and 633. Thus, sample number 3 is between 5 and 24 times more mutagenic than sample 2.

During the 1981-82 study, two additional samples were collected downstream from a Deutz diesel without any catalytic converter in the hopes of learning which of the 1980-81 results was correct, i.e., to obtain a more reliable estimate of the mutagenicity of the exhaust from a bare Deutz diesel. Unfortunately, the mutagenicity of samples 4 and 5 were also very different. The specific mutagenicity of these two samples (0.39 and 11.2) differed by approximately 30 times and the maximum and average revertants/m^3 in the air downstream from this diesel (4882 and 334, and 3621 and 181, respectively) differed by factors of 15 and 20, respectively.

The specific mutagenicity, the maximum and the average revertants/m^3 for sample 5 are all much higher than those found in samples 2-4. In fact, the average value for the average revertants/m^3 for samples 2-4 is 280 $\pm$ 315. The average value of 280 is 11 standard deviations away from the 3621 revertants/m^3 found for sample 5 and thus sample 5 is statistically different from the others. The same conclusion is reached if one considers the maximum revertants/m^3. The average for sample 2-4 is 480 $\pm$ 384 and the 4882 found for sample 5 is 12 standard deviations away from the average. Again sample 5 is found to be statistically different. Finally, the specific mutagenicity of sample 5 is three standard deviations away from the average specific mutagenicity for samples 2-4. Thus, sample 5 is statistically different at the 99.7% confidence level. As a result, the best estimate for the specific mutagenicity, the maximum revertants/m^3 and the average revertants/m^3 downstream from a bare Deutz diesel would

seem to be 2.1, 480 and 280, respectively.

If we were to use the best estimate for the bare Deutz engine, the air containing the diesel exhaust is six times more mutagenic than the air in the fresh air raises. This indicates that the exhaust is mutagenic when it is emitted from the diesel engine.

A second and perhaps more sensible approach however, is to try to discover why the mutagenicity of these four samples are so different, i.e., to try to relate the mutagenicity of the exhaust to some differences in the samples. When one examines the sampling sites and duty cycle of the diesel for samples 2-5, one finds that the Hi Vol samples 2-4 were collected near the dump site. Thus, most of the diesel particulate collected on these filters would have been released at or near the dump site[1] when the diesel was not under full load. Sample 5, however, was collected near the muck pile where the diesel was working at maximum load. Since the PAH concentrations and the percent CO_2 are usually higher at a mucking site than in a tramway or near a dump site, it is not surprising that the mutagenicity of the air collected near a muck pile is also higher. This would occur because more diesel particulate, which is mutagenic (vide supra), would be released in the same volume of air at a mucking operation. Thus, greater amounts of mutagenic material would be collected in the same time and a higher mutagenicity would be found.

In fact, the mutagenicity of the air downstream from a diesel is more mutagenic when the diesel is under a heavy load as samples

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[1] PAHs and probably nitro PAHs travel through the air for very short distances in humid nickel mines with curved drifts.

2-5 and 8-13 (vide supra) suggest. One will have to be very careful in determining the PAH concentrations and the mutagenicity associated with a particular piece of equipment, or exhaust treatment device or mining operation. Obviously, a wide range of operating conditions will have to be assessed when a new piece of mining equipment is being tested.

It is worth commenting on the relative mutagenicity of samples 2 and 3. The average duty cycle for sample 2 was longer than that for sample 3 because ore was drawn from a more remote area of the mine for a portion of the number 2 sampling period. This would obviously reduce the amount of diesel particulate and thus the amount of carcinogens that could be collected on the filter. As a result, one would expect the lower mutagenicity in sample 2 and this is what is found. Although the mutagenicity and NO_2 levels are lower for sample 2, the percent CO_2 and PAH levels are higher for sample 2 than they are for sample 3. As a result, it is difficult to know whether our interpretation of the results is correct.

The average revertants/m^3 for the Deutz engine fitted with a PTX catalytic converter are higher than the best average values for a Deutz diesel with no exhaust treatment devices. In fact, adding a PTX catalytic converter to a Deutz diesel increases the maximum revertants/m^3 from 480 to 691 (by 44%) and the average revertants/m^3 by 66%, i.e., from 280 to 465. The specific mutagenicity is also 62% higher for the sample collected downstream from the diesel with the PTX catalytic converter. It is worth noting that the PTX samples were not collected near the muck pile. This means that the ratios calculated using the averages from samples 2-4 can be used to

estimate the effect of adding a PTX catalytic converter to the exhaust system of a Deutz diesel.

The PAH concentrations are also higher from the Deutz diesel with the PTX catalytic converter. The Total PAHs are 13% higher, the Total - pyrene are 21% higher and the Total Carcinogenic PAHs are 103% higher from the diesel fitted with the PTX. It is worth noting that both the mutagenicity and PAH concentrations are higher when a PTX catalytic converter is used in spite of the fact that the diesel exhaust was more dilute in the PTX experiments. This conclusion is warranted because the CO_2 concentration is lower in the PTX experiments than in any of the experiments where the exhaust was collected downstream from the bare engine. Thus, one can conclude that the PTX catalytic converter increases the mutagenicity of the exhaust probably by providing a site for the nitration of PAHs. The greater amount of nitration may occur because the PTX catalyzes the conversion of NO to NO_2. A higher NO_2 concentration would increase the rate of reaction between PAHs and NO_2 in the hot exhaust gases. This would obviously increase the amount of nitro PAHs, equation 1, page 40, and thus, the mutagenicity of the exhaust.

The 1980-81 study indicated that the exhaust collected downstream from a Deutz engine fitted with a Dieseler III catalytic converter was approximately 12 times more mutagenic (samples 8 and 9) than the exhaust from either a bare Deutz engine or a Deutz with a PTX catalytic converter in the exhaust train (11). This result was surprising because the Dieseler III and the PTX converters are both platinum catalysts. As a result, several more samples were collected downstream from a Dieseler III catalytic converter during the

1981-82 study in order to learn whether the particulate released from a Dieseler III catalyst really was more mutagenic than the particulate emitted from other exhaust treatment devices.

The results obtained from samples 9-13 have confirmed that the particulate from the Dieseler III catalytic converter is much more mutagenic. In fact, the samples collected downstream from the Dieseler III are more mutagenic than any of the samples collected near a Deutz diesel.

There are problems in expressing the increase in the mutagenicity resulting from the introduction of the Dieseler III catalyst however, because the mutagenicity of the exhaust is very different when the samples are collected under different conditions. For example, the average values of the maximum and average revertants/m^3 for samples 8-11 are 5698 and 4340 respectively. The corresponding averages for all six Dieseler III samples are approximately three times higher, i.e., 16,854 and 12,895. If the averages for samples 8-11 are used, the exhaust from the Dieseler III catalyst is approximately 14 times more mutagenic than that from the bare diesel and 9 times more mutagenic than the exhaust from a Deutz engine fitted with a PTX catalytic converter. If the averages for samples 8-13 are used, the exhaust from the Dieseler III is approximately 40 times more mutagenic than the exhaust from a bare diesel and 26 times more mutagenic than the exhaust from a PTX catalyst. Even if the total average for samples 2-5 is used for the bare diesel, the Dieseler III exhaust is still approximately 13 times more mutagenic than the exhaust from the bare diesel. Thus, whatever averages are used, the exhaust from the Dieseler III is at least ten times more mutagenic

than that obtained from any other configuration we have tested.

The average PAHs are also higher downstream from the Deutz fitted with a Dieseler III catalyst. For example, the average Total PAHs are 2.9 times higher, the Total - pyrene are 1.8 times higher and the Total Carcinogenic PAHs are 2.6 times higher than those from the bare engine and 2.5 times, 1.5 and 1.3 times higher, respectively, than those from a Deutz with a PTX catalytic converter. Although both the PAHs and the mutagenicity of the extract from a filter collecting the exhaust from a Dieseler III catalyst, are high, one can not place any faith in the averages calculated above because the PAH concentrations and the mutagenicity vary widely with sampling site and the portion of the duty cycle that is monitored. For example, the PAHs are more concentrated in samples 10-13, which were collected near the muck pile and lower in the samples (8 and 9) collected at the dump site. The Total PAHs, Total - pyrene and Total Carcinogenic PAHs are 4.1, 4.9 and 9.3 times respectively, higher near the muck pile than they are at the dump site. The mutagenicity also varies with the portion of the duty cycle that is monitored. Since the average mutagenicity of samples 10-13, which were collected at a mucking site, is higher than that for samples 8 and 9, it would appear that the exhaust collected near a muck pile is more mutagenic. The relationship between the mutagenic response and the duty cycle is more complex however, because the extracts from samples 8 and 9 (dump site) are equal to those collected near a mucking operation (samples 10 and 11). Two possible explanations for these differences in PAH concentrations and mutagenic response are presented below.

The higher PAHs near the mucking operation can be explained

in two ways. One explanation is that the PAHs in the exhaust are an unburned residue of the PAHs in the fuel. Since more fuel is burned when the diesel is working hard mucking ore, more PAHs would be released per unit time (volume of air) during the mucking operation and their concentration would therefore be greater in the mine air. The second possibility is that the Dieseler III catalyst traps the particulate when the diesel is working at low load, i.e., during the traming and dumping portion of the duty cycle, and releases it when the diesel is under maximum load at the muck pile. If this were the case, most of the PAHs would be released at the muck pile and the PAHs would be much more concentrated in samples collected at this point. If this hypothesis were correct, the extract from the filter should also be more mutagenic at the muck pile. This would be expected because the particulate (PAHs) released in the traming and dumping portion of the duty cycle would be held at a high temperature in the catalyst. Since the PAHs would be exposed to NO_2 in the catalyst, they could react with NO_2 to form nitro PAHs and the mutagenicity of the exhaust released at the muck pile could be greater. Although these catalysts have been reported to store particulate at low load and release it under high load conditions (18), several factors suggest that this is not the major mechanism. For example, the PAHs are volatile and are not quantitatively trapped by the particulate. Thus, it is unlikely that the PAHs would be retained by the catalyst. Moreover, the mutagenicity of samples 10 and 11 (collected near the muck pile) is equal to the mutagenicity of samples 8 and 9 which were collected at the dump site. This is not consistent with the latter explanation and it would appear that the former

hypothesis is correct. If the PAHs are more concentrated near the muck pile because more PAHs are released per minute (m^3 of air) at this site then it appears that the mutagenicity of the samples is determined in part by the NO_2 concentration. Samples 8 and 9 were collected near a dump site where the diesel was at low load. The NO_2 concentration at this site was slightly higher than average, i.e., the average NO_2 concentration near a diesel in this mine is 0.8 ppm. Thus, a significant portion of the PAHs would be converted into nitro PAHs in the engine and/or exhaust system and a reasonably high mutagenic response would be expected.

Samples 10-13 on the other hand, were collected close to a mucking operation and should have higher concentrations of PAHs and perhaps a higher mutagenic response because more fuel would be burned per unit time when the diesel was working hard mucking ore. While the PAH concentrations in samples 10-13 are higher as one would expect, the mutagenicity of samples 10 and 11 is equal to those found at the dump site. However, the NO_2 concentration was unusually low (0.3 ppm) at the sampling site for samples 10 and 11. Since the formation of the nitro PAHs obviously depends on the concentration of NO_2, very few of the PAHs in samples 10 and 11 would be converted into nitro PAHs. Since almost all of the mutagenic activity in the exhaust is due to the nitro PAHs (see Table 23), samples 10 and 11 would be expected to have an unusually low mutagenicity for samples collected near a mucking site.

Samples 12 and 13 which were also collected near a mucking site, are approximately 3 times more mutagenic than samples 10 and 11. If the NO_2 concentration was normal (0.8 ppm) when samples 12 and 13

were collected, more of the PAHs would have been converted into nitro PAHs in the diesel and/or exhaust train and a higher mutagenic response would be found. Although the actual NO_2 levels were not obtained at these sampling sites, it is worth noting that both the expected NO_2 concentrations and the mutagenicity of samples 12 and 13 are approximately 3 times higher than those found in samples 10 and 11. This would be expected if the above hypothesis were correct.

Although the PAH concentrations and mutagenicity of the exhaust at the different sampling sites can be rationalized, we are unable to explain why the exhaust emitted from the Dieseler III catalyst is so much more mutagenic than the exhaust from the bare diesel or the PTX catalyst. In spite of this problem, this study has clearly demonstrated that the Dieseler III catalytic converter increases the mutagenicity and the PAH concentrations in the diesel exhaust markedly. This obviously means that the Dieseler III catalyst is not the catalyst of choice, if indeed, a catalyst is used at all. In fact, since both the PTX and Dieseler III catalysts increase the PAHs and the mutagenicity of the exhaust, increase the NO_2/NO ratio, increase the amount of sulfuric acid mist (39,40), and probably increase the amount of oxygenated hydrocarbons such as aldehydes, in the exhaust, the authors do not believe that the extra expense related to purchasing and maintaining these devices is warranted. The only real advantage of the catalytic converters is to reduce the CO and the unburned aliphatic hydrocarbons. Since CO is not a problem from an industrial health point of view, and the aliphatic hydrocarbons can be metabolized safely by the body, it is difficult to understand why catalytic converters are used in

underground mines.

Finally, it is worth noting that the specific mutagenicity of the exhaust extract is not constant for a particular type of diesel. The specific mutagenicity of the bare Deutz diesel varies from 0.35 to 11.2 or by more than 30 times. Although the specific mutagenicity of the exhaust is more constant for the Deutz diesel fitted with the Dieseler III catalyst, the specific mutagenicity of samples (8-13) still varies from 27 to 121, i.e., by a factor of 4.5. The wide variation that is observed in these specific mutagenicities indicates that the specific mutagenicity is not always the same for a particular type of diesel but depends on several other factors such as the NO_2 concentration and the load on the diesel. This observation is important because researchers in the United States have used the specific mutagenicity of the exhaust to characterize a particular type of diesel and exhaust treatment system, i.e., they believe that the specific mutagenicity of the exhaust is always the same for a particular type of diesel. The work we have done suggests that this is only true if special precautions are taken, i.e., if the exhaust was always collected under exactly the same load and environment.

The next set of samples, 14 and 15, were collected under different conditions than samples 2-13. Samples 2-13 were collected in a nickel mine where the NO_2 concentration was an average of 0.8 ppm and Deutz diesels were used. In the salt mine where samples 14 and 15 were collected, Caterpillar diesels fitted with PTX catalytic converters[1] were used and the NO_2 concentration in the

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[1] One of the trucks was fitted with fume diluters. The front end loader and the other two trucks had PTX or PTX type catalytic converters in the exhaust system.

mine air was between 3.5 and 4.0 ppm or approximately 5 times those found in the nickel mine. These samples were of interest because the results would indicate whether the nitro PAHs formed in the mine environment, i.e., in the mine air or on the filter, or whether the nitro PAHs are formed in the diesel, i.e., in the combustion chamber, the catalytic converter or in the hot gases in the exhaust system.

If the nitro PAHs are formed in the combustion chamber and/or exhaust system of the diesel, the concentrations of the nitro PAHs and thus the mutagenicity of the exhaust extracts should be similar in the two mines because the nitro PAHs would be formed under similar conditions in the two diesels. This conclusion is warranted because the mutagenicities of the exhaust from the Deutz and Caterpillar diesels are quite close, Table 30. Thus, the fact that different diesels are used in the two mines should not have a major effect on the results.

If the nitro PAHs are formed in the mine air and/or on the filter, the nitro PAHs should be much more concentrated in the salt mine. The NO_2 concentration is approximately five times higher (3.75/0.8) than that observed in the nickel mine. Increasing the NO_2 concentration of one of the reactants required in the formation of the nitro PAHs by five times should increase the rate of formation of the nitro PAHs by five times. The results in Table 28 also show that the Total PAHs are (360/32.4) eleven times more concentrated than they were in the nickel mine where a Deutz diesel fitted with a PTX catalytic converter (samples 6 and 7) was monitored. Since increasing the concentration of the other reactant required in the

TABLE 30 - The specific mutagenicity of Caterpillar and Deutz Diesels[a]

Engine	Source	Specific Mutagenicity TA-98-S9
Caterpillar 3304	E.P.A.	0.3
Caterpillar 3208	J. Johnson	0.61 to 0.74
Deutz 6L714	Ontario Research Foundation	0.34
Deutz 6L714	This Report[b]	0.35,0.39 5.6
Caterpillar 3208 + PTX	J. Johnson	1.3 to 2.2
Deutz 6L714 + PTX	Ontario Research Foundation	3.9
Deutz 6L714 + PTX	This report	2.7,4.0

[a] Some of the data in this Table was supplied by P. Mogan, CANMET, 555 Booth St., Ottawa, Ontario.

[b] The result from sample 5, Table 28, was not included because it was collected near a muck pile where the diesel was under full load.

formation of the nitro PAHs would also increase the rate of reaction, the rate of formation of the nitro PAHs in the mine environment would be at least 50 times higher in the salt mine. Thus, the amount of nitro PAHs should be much higher in the air in the salt mine and the exhaust would be approximately 50 times more mutagenic than the exhaust obtained in the nickel mine.

The average specific mutagenicity, maximum revertants/m^3 and average revertants/m^3 of the diesel exhaust collected downstream from a Caterpillar 1693 front end loader and three Caterpillar 3306 diesel trucks fitted with PTX catalytic converters in the salt mine, Figure 4, were only $\frac{2.5}{3.4}=0.74$, $\frac{1241}{691}=1.8$ and $\frac{1051}{465}=2.3$ (an average of 1.6) times higher than the corresponding averages for the exhaust samples collected downstream from a Deutz diesel fitted with a PTX catalytic converter in the nickel mine. Obviously, the exhaust samples collected in the salt mine are not significantly more mutagenic than those found in the nickel mine. In fact, when one considers that three trucks and one front end loader were used in the development heading in the salt mine, the exhaust collected from a single diesel in the NO_2 polluted air in the salt mine may not be as mutagenic as that collected from the single diesel in the nickel mine. This means that the nitro PAHs are primarily, if not completely, formed during the combustion in the diesel and/or in the exhaust system and little or none of the nitro PAHs are formed in the mine air or on the filter. It is worth noting that this conclusion is supported by the work of Butler and Crossley (41). These workers found that the reaction between PAHs and NO_2 is very slow at room temperature. This result is important because it indicates that the work to reduce

or eliminate the nitro PAHs from the mine environment must be focussed on the diesel and its exhaust treatment system. This means that the effect of different fuels, which reduce the PAH concentration, and the engine or catalyst design are areas of future research.

The next set of experiments involved determining the mutagenicity and PAH concentrations in the extract from diesel exhaust collected downstream from a bare (operating without any catalytic converter) 8V71 Detroit diesel in an uranium mine. This study was undertaken because Zweidinger (16) reported that the exhaust from a 2-cycle Detroit diesel engine in a 1977 model city bus had a specific mutagenicity of only 0.02, i.e., the exhaust from the Detroit diesel is between 1/15 and 1/280th as mutagenic as the exhaust from bare Caterpillar and Deutz diesels, Table 30. Thus, it was important to determine whether the exhaust from the 8V71 Detroit diesels used in underground mines also gave a very low mutagenic response.

The mutagenicity of the exhaust extract from the Detroit diesels (samples 16 and 17) is very low. In fact, a negative Ames response was obtained from both samples. It must be noted however, that this negative response does not mean that the exhaust from the Detroit diesel is not mutagenic. It only indicates that it is much less mutagenic than the exhaust from either the Deutz or Caterpillar diesels. In fact, one of the Detroit diesel samples was collected approximately 25 feet behind the diesel when it was mucking ore so that this sample was collected closer to the muck pile than any other sample reported in Table 28. Since the exhaust collected near the muck pile is more mutagenic (samples 5, 12 and 13), the difference

between the mutagenicity of the exhaust from the Detroit diesel and those from the other diesels would be even greater if the samples were collected equal distances from the diesel. As a result, one must conclude that the exhaust from the Detroit diesel is much less mutagenic than the exhaust from other diesels we have tested. This suggests that there are little or no nitro PAHs in the exhaust from a bare Detroit diesel engine. It would be interesting to do Ames and PAH work on a Detroit diesel with PTX catalysts to demonstrate more clearly how these catalysts affect the PAH concentrations and mutagenicity of the exhaust.

The results of the PAH analyses were surprising. The PAH concentrations in the exhaust from the Detroit diesels were very high. In fact, the average Total PAHs, Total - pyrene and Total Carcinogenic PAHs are within experimental error of the highest levels in Table 28 (see samples 14 and 15) and since these levels have been found from a single diesel rather than the three trucks and a front end loader that were used in the development heading where samples 14 and 15 were collected, extremely high concentrations of PAHs are released from this Detroit diesel. This result is very surprising and somewhat disturbing because we had believed that the PAH levels and the mutagenicity were related. However, the results from the Detroit diesels as well as those from the oil mist released in the drilling operations sample 18, Table 28, obviously indicate no such relationship exists. This is confirmed because the correlation coefficients for plots of the specific mutagenicity and the average revertants/m^3 against the Total PAHs found downstream from diesels in underground mines (samples 2,3,6-17) are less than 0.28.

In fact, the correlation coefficient for the least squares line of a specific mutagenicity - Total PAHs plot for the only set of results collected downstream from the same diesel operating in the same mine, i.e., from sample 8-13 collected downstream from a Deutz diesel fitted with a Dieseler III catalytic converter in nickel mine I, is only 0.45. This also indicates that the Total PAHs are not related to the nitro PAHs (the mutagenic response) even when the same diesel is monitored in the same mine. When the average revertants/m^3 are plotted against the Total PAHs, Figure 5, the correlation coefficient of the best straight line is 0.86.

However, the Total PAHs for the four points at the left side of Figure 5 are very different while the average revertants/m^3 are virtually identical and thus it is hard to believe that these two properties of the exhaust extracts are really related.

However, an interesting correlation is found when the data in Figure 5 is considered in another way. The correlation coefficients for four of the points is 0.9998 (dotted line). These four points (⊙) have been considered together because these samples were probably collected when the NO_2 concentrations were the same, i.e., close to 0.8 ppm. The other two samples (⊣) were collected when the NO_2 concentration was far below normal, i.e., 0.3 ppm. If the conversion of PAHs into nitro PAHs depends on the NO_2 concentration as one would expect, then fewer of the PAHs would have been converted into nitro PAHs and the mutagenicity would be lower and the Total PAHs higher. It is interesting that this is exactly why these points are off the 0.9998 correlation coefficient line, i.e., the Total PAHs are too high for the average revertants/m^3. Unfortunately, we do not have enough data to tell whether the Total PAHs are related to the average revertants/m^3 when samples are collected under the same conditions and it remains

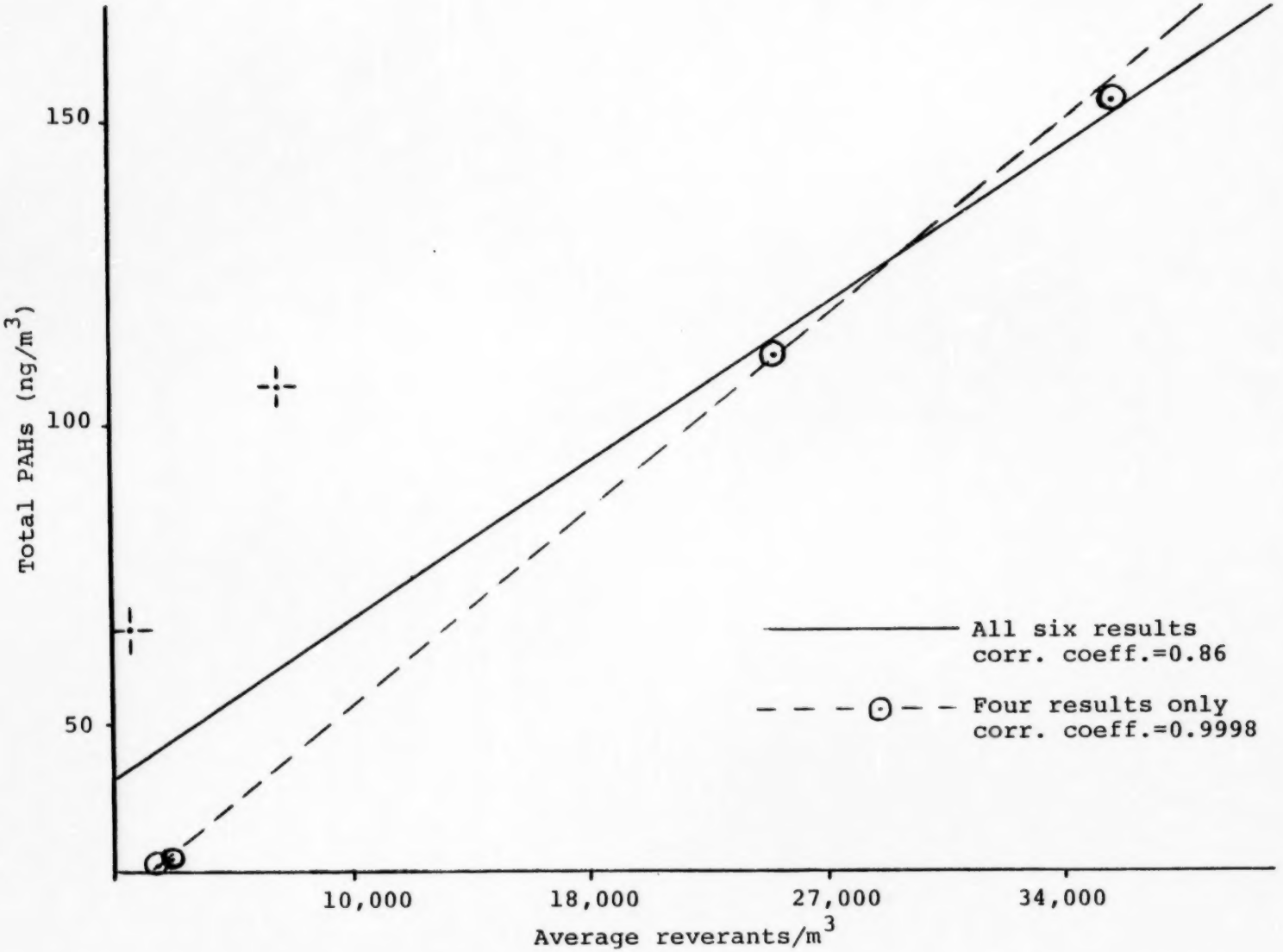


Figure 5. The Total PAHs and average revertants/m^3 found downstream from a Deutz diesel fitted with a Dieseler III catalyst in a nickel mine.

an interesting hypothesis at this time.

In conclusion, the mutagenicity (nitro PAHs) is obviously not related to the Total PAHs in underground mines, i.e., when samples are obtained from different diesels in different mines. Moreover, the mutagenicity does not appear to be related to the PAHs even when samples are collected downstream from the same engine working in the same mine. However, the PAHs and nitro PAHs may be related when samples are collected from the same engine in the same mine if the NO_2 concentrations are the same.

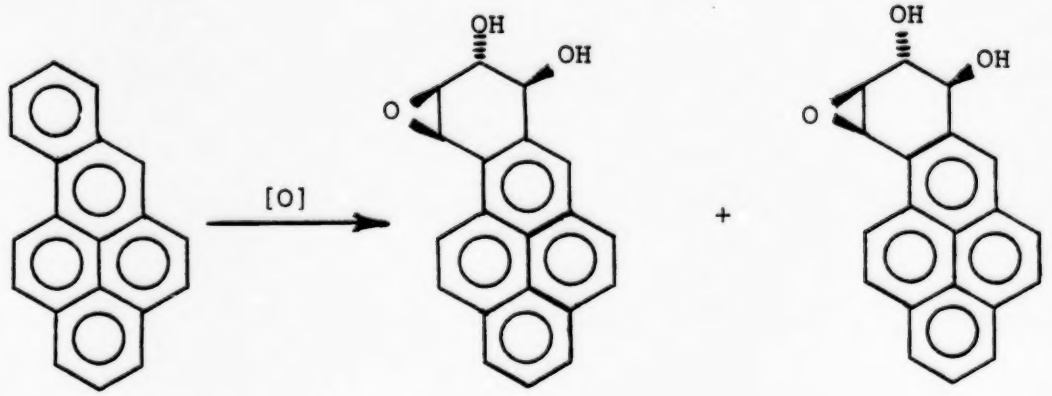
The results from samples 2-17 in Table 28, obviously mean that the Ames bioassay and PAH analyses are assessing different portions of the exhaust. The results in Table 23 and Horton's work with the nitroreductase-deficient Salmonella strains (strains that do not react with nitro PAHs)(38), indicate that the Ames assay only responds to the nitro PAHs in the exhaust. The PAH analysis on the other hand, monitors thirteen polynuclear aromatic hydrocarbons and does not identify or quantitate any of the nitro PAHs. Thus, the Ames bioassay and the PAH analysis monitor a different group of compounds in the diesel exhaust and give a completely different insight into the health effects of this very complex mixture.

Finally, since the concentrations of these two classes of compounds are not related in the diesel exhaust one will have to do both Ames bioassays and PAH analyses if one wishes to determine the complete health effects of diesel exhaust (vide infra).

On first considering the results obtained from the Detroit diesel tests one might conclude that the Detroit diesel is the diesel of choice in the underground mines. However, this conclusion is not warranted. Although the mutagenicity of the exhaust is very low and

the nitro PAHs are only present in very low concentrations in the exhaust from a Detroit diesel, the exhaust very high concentrations of PAHs. Moreover, the concentrations of the carcinogenic PAHs are significantly greater than those found in the exhaust from other diesels. Since the PAHs are in the vapour state, or on respirable sized particulate, miners working on or near the diesel are exposed to known carcinogens in a respirable form. Thus, the results obtained from the Detroit diesel do not solve the problem from an industrial health point of view because no one knows whether to choose the Detroit diesel which emits the lowest concentrations of nitro PAHs but very high concentrations of the potential carcinogens (PAHs), or the Deutz deisel which emits reasonably low concentrations of PAHs (potential carcinogens) and the mutagenic nitro PAHs.

The results with the nitroreductase-deficient Salmonella strains demonstrates that the PAHs in the exhaust do not give a positive response in the Ames test. This may occur for two reasons. First, the PAHs are usually not highly mutagenic or carcinogenic (42). Thus, large concentrations of the PAH are required to give a positive response in the Ames bioassay. For example, the concentration of benzo(a)pyrene is too low in the extracts from diesel exhaust samples collected underground to give a positive response in the Ames test (43). Other work (44-46) has shown that the PAHs themselves are not the active form of the PAH, i.e., they are not the ultimate carcinogen (the compound that actually initiates the cancer). For example, benzo(a)pyrene is metabolized (converted) into a pair of benzo(a)pyrene-7,8-diol-9,10-epoxides (A and B), equation 2 in the body and these are the ultimate carcinogens that initiate the



A B

cancer (44-46).

Thus, although benzo(a)pyrene and the other "carcinogenic" PAHs are not potent enough or present in high enough concentration[1] to trigger a positive response in the Ames bioassay, the presence of these compounds in the mining environment is still of concern because they can be metabolized into potent carcinogens in the body. Thus, the negative response from the PAHs in the Ames bioassay does not reduce the concern from a health point of view. In fact, the concern arises because i) several workers (47-49) have found that the particulate remains in the lungs of mice for several months after the exposure to diesel exhaust has ceased, and because ii) workers (9) have demonstrated that PAHs are retained in the body for much longer times when they are adsorbed on particulate matter. Thus, the PAHs will be retained in a miner's lungs for several months. This obviously increases the probability that the PAHs will be metabolized to the ultimate carcinogen and induce cancer before they are

[1] The Hi Vol filters were frozen as soon as possible and stored in the dark. Since the PAHs are stable under these conditions, they were recovered and analyzed before they could be converted into their more reactive metabolite.

removed from the lungs.

Obviously, more research is needed to find ways of reducing the concentration of both the nitro PAHs and the PAHs in the diesel exhaust. If the nitro PAHs are formed from PAHs in the engine and/or the exhaust system of the diesel, and if the PAHs are an unburned residue of the PAHs in the fuel, as the authors believe (vide infra), removing the PAHs from the fuel would solve both problems, i.e., eliminate both the nitro PAHs and the PAHs from the diesel exhaust. Other work would involve determining how changes in engine design and/or in exhaust treatment devices affect the concentrations of both classes of compounds in the exhaust. Obviously, both groups of compounds will have to be monitored if one wishes to prove that the exhaust from a particular diesel is less hazardous.

Finally, the results from the oil mist and blasting experiments have been included in Table 28. The oil mist sample is non-mutagenic, presumably because the oil does not contain any nitro PAHs. However, this sample is high in PAHs (potential carcinogens) and is therefore of concern from an industrial health point of view.

Extremely high concentrations of both the PAHs and the nitro PAHs (mutagenic response) are present in the air downstream from a blast when Amex (diesel fuel- ammonium nitrate) explosive is used. For example, the maximum revertants/m^3 and the average revertants/m^3 are 2.3 and 3.1 times respectively, higher than the highest values found downstream from a diesel engine (sample 13) and are 175 and 239 times higher than the average response for the exhaust from a Deutz diesel fitted with a PTX catalytic converter (the most common diesel found in Canadian mines).

The PAH concentrations are also unusually high in the air downstream from an Amex blast. For example, the Total PAHs, the Total - pyrene and the Total Carcinogenic PAHs are 4.8, 7.6 and 11 times, respectively, higher downstream from a blast than the highest PAH concentrations downstream from a diesel and are 73, 65 and 58 times respectively, higher than the corresponding values downstream from a Deutz diesel fitted with a PTX catalytic converter. These results will not be discussed in detail in this section because they have been considered earlier in the report. They have simply been included so that the PAH concentrations and the mutagenic response of these materials can be compared to those found for diesel exhaust.

The Influence of Fuel on the PAH Levels in Underground Mines

Some of our previous work has suggested that the PAHs in the exhaust from diesels are mainly, if not completely, an unburned portion of the PAHs in the original fuel (2,11,13). As more work has been done on the PAH levels in dieselized underground mines, this relationship has become more and more obvious. Although some work suggests that the PAHs are generated from other molecules during the burning process (51,52), the PAH analyses of Hi Vol samples collected downstream from diesels working in five different mines in five different communities indicate that the PAHs in the fuel play an important role in determining the distribution and amount of PAHs in the exhaust. The evidence for this suggestion is presented below.

Hi Vol samples collected downstream from a diesel in five different mines situated in five different communities have been analyzed for PAHs. In each mine the diesel fuel has been supplied by

different companies. Two of the mines are in completely different areas of Canada from the three mines where most of the samples were collected and would obviously be using different fuels. A different grade of fuel was used in the two mines that were in the same area. The last mine was supplied from a different distribution center so that this fuel would be different from the others. As a result, the diesel fuels burned in the mines we have sampled are different.

Table 31 gives the average concentrations of the PAHs found in the different exhaust samples collected in the five different mines. An examination of the concentrations of the individual PAHs shows that there are striking differences in the concentrations of the individual PAHs. For example, the highest concentrations of pyrene, benzo(a)anthracene, benzo(e)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenzo(def,mno)chrysene and benzo(rst)pentaphene were found in salt mine I where a Caterpillar diesel was used. The highest concentrations of fluoranthene, perylene and benzo(a)pyrene on the other hand, were found in the samples collected in an uranium mine where Detroit diesels were used. The highest dibenzo(a,h)anthracene and naptho(1234,def)chrysene concentrations were found in the other salt mine (mine II) where Caterpillar diesels were used. In fact, dibenzo(a,h)anthracene was only found in the exhaust sample collected in two mines, salt mine II and the uranium mine. Finally, the sample collected in salt mine I has the lowest concentrations of benzo(a)pyrene and perylene even though it has the highest concentration of most of the other PAHs.

Obviously, the PAH levels and distribution are very different in the different mines. Unfortunately, these results are not

TABLE 31 - A comparison of the PAH concentrations in five different mines using different fuels

	Concentration in ng/m^3				
	Average Caterpillar Salt Mine I	Salt Mine II	Average Deutz Nickel Mine I	Nickel Mine II	Average Detroit Uranium Mine
Pyrene	280	127	34.3	124	184
Fluoranthene	13.5	21.8	3.45	9.25	33.0
Benzo(a)anthracene*	22.4	9.86	4.42	8.58	17.1
Benzo(e)pyrene	32.1	27.8	11.9	14.5	29.2
Perylene	0.19	0.35	0.32	0.32	0.85
Benzo(k)fluoranthene	6.81	3.56	2.00	1.51	3.66
Benzo(a)pyrene*	0.58	1.63	1.63	1.24	2.50
Benzo(ghi)perylene*	8.96	4.78	6.90	2.08	8.62
Dibenzo(a,h)anthracene*	0	2.70	0	0	1.95
Dibenzo(def,mno)chrysene	0.53	0.52	0.40	0.50	0.32
Naptho(1234,def)chrysene*	8.98	12.4	3.60	3.26	6.54
Benzo(rst)pentaphene*	2.66	0.78	0.64	0.39	0.52
Total PAHs	377	213	73.1	166	288
Total-pyrene	96.8	86.2	38.8	41.4	104
Total Carcinogens	43.6	32.2	19.5	15.6	37.2

* Carcinogenic PAH

conclusive because the samples were obtained in different mines where different diesels were used. Moreover, we were not able to ensure that the diesels were equally well maintained. In spite of these shortcomings, significant differences in the PAH concentrations and in the distribution of PAHs in the exhaust are apparent and one must conclude that the diesel fuel and/or the type of diesel affect the composition and amounts of the PAHs in the exhaust markedly.

Comparing the results from two mines where the same type of ore is mined and the same type of diesel are used suggests that it is the fuel rather than the type of diesel that is the major factor in determining the PAH distribution in the exhaust. When one compares the PAH concentrations in the exhaust samples collected in the two salt mines where the water-cooled Caterpillar diesels were used, columns 1 and 2 of Table 31, one sees very large differences in the PAH concentrations. For example, while the pyrene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(ghi)perylene, benzo(rst)pentaphene, and the Total PAHs are two to three times more concentrated in mine I than in mine II, fluoranthene and naptho(1234,def)chrysene are 1.5 times more concentrated and benzo(a)pyrene is 3 times more concentrated in salt mine II. Moreover, the total absence of dibenzo(a,h)anthracene in the air in mine I is a striking difference. Since the types of mines and types of diesels are the same, these differences can almost certainly be attributed to the fact that different fuels were used in the two mines. Although we have not been able to analyze the PAHs in the fuels used in these two mines, we do know that the diesel fuels were obtained from different crude oils which have very different properties and undoubtedly different

amounts and distributions of PAHs.

Similar differences are found in the exhaust samples collected in the two nickel mines where Deutz diesels were used. A comparison of these results, columns 3 and 4, Table 31, show that pyrene, fluoranthene, benzo(a)anthracene, and the Total PAHs are significantly (two to four times) more concentrated in the air in mine II. Benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, naptho-(1234,def)chrysene, benzo(rst)pentaphene and the Total Carcinogenic PAHs on the other hand, are between 10 percent and 3.3 times more concentrated in nickel mine I. Again, since the mines and types of diesels are the same and the fuels are different, i.e., a different (less refined - higher sulfur) grade fuel was used in nickel mine II, one is forced to conclude that the fuel is the most likely source of the difference.

Other results (21) also suggest that the PAHs in the exhaust are determined by the PAHs in the fuel. The results in Table 32 compare the average PAH concentrations in the exhaust in a nickel mine with the PAH concentrations in a fuel sample collected near the same time. The PAHs found in the fuel and exhaust samples collected during the 1979-80 sampling period are given in columns 1 and 2 of Table 32, while the PAHs found in the fuel and exhaust samples collected during the 1980-81 sampling period are shown in columns 3 and 4. The ratio of the (PAHs in the 1980 fuel / PAHs in the 1981 fuel) samples are 0.18, 0.16 and 0.18 for the Total PAHs, the Total - pyrene and the Total Carcinogenic PAHs, respectively. The corresponding ratios for the average PAHs in the exhaust samples are 0.45, 0.28 and 0.23. Thus, the decrease in the fuel PAHs is almost

TABLE 32 - A comparison of the PAHs in the fuel and in the exhaust samples collected in the 1979-80 and 1980-81 sampling periods

	PAH concentration in µg/kg of Diesel Fuel Summer 1980	Average PAH concentration in ng/m^3 in Diesel Exhaust Winter&Spring 1979-80	PAH concentration in µg/kg of Diesel Fuel Spring 1981	Average PAH concentration in ng/m^3 in Diesel Exhaust Winter&Spring 1980-81
Pyrene	1.65	38.7	0.39	33.3
Fluoranthene	1.25	10.9	0.13	3.45
Benzo(ghi)perylene*	1.16	21.3	0.14	3.58
Benzo(e)pyrene	0.69	22.4	0.14	9.44
Benzo(a)anthracene*	0.32	16.4	0.05	4.42
Naptho(1234,def)chrysene*	0.14	7.65	0.09	2.67
3-Methylcholanthrene*	0.04	0	0.01	0
Benzo(a)pyrene*	0.01	5.40	0.005	0.76
Benzo(k)fluoranthene	0.01	5.98	0.003	1.08
Perylene	0.004	1.01	0.001	0.13
Dibenzo(def,mno)chrysene	0.001	1.41	0.001	0.17
Benzo(rst)pentaphene*	0	1.44	0	0.46
Total PAHs	5.28	133	0.96	59.4
Total-pyrene	3.63	93.9	0.57	26.1
Total Carcinogens	1.67	52.2	0.30	12.0

* Carcinogenic PAH

exactly paralleled by the decrease in the PAHs in the exhaust. This obviously suggests that the PAHs in the exhaust are related to (determined by) the PAHs in the fuel. Unfortunately, only one fuel sample was obtained in each year and the fuel samples were not obtained at the time any particular test was run. While these factors obviously reduce the value of this data, the results certainly are consistent with the hypothesis that the fuel has a strong influence on the PAHs in the exhaust.

Finally, the relationship between the PAHs in the exhaust and those in the fuel can be demonstrated in another way (21). Table 33 ranks the twelve PAHs found in the fuel sample collected in 1980 and 1981, in decreasing concentration. For example, the most concentrated PAH in the fuel, pyrene, was given number 1 and the least concentrated PAH was given number 12. The average concentration of the individual PAHs in the exhaust samples collected in the 1979-80 and 1980-81 sampling periods were also ranked in the same way. When the order of the PAHs in the fuel is compared with the order of the PAHs in the exhaust samples collected close to the time when the fuel was obtained, 14 of 24 or 60% of the PAH comparisons have the same order within one unit, in the exhaust and in the fuel. Of the remaining 10 comparisons, the order differs by two for five of the PAHs and by three for three more of the PAHs. Thus, 19 of 24 PAHs or 80% agree within two units and 22 of 24 (92%) agree within three units.

Only in two cases, do the orders fail to agree. This is with 3-methylcholanthrene which is not found in the exhaust samples. This result might have been anticipated because the 3-methylcholanthrene would not be expected to be as stable as the other PAHs, i.e., the

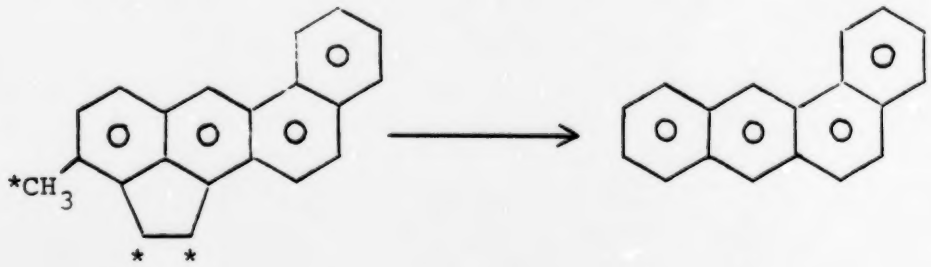
TABLE 33 - The relative concentrations of PAHs in the diesel fuel and diesel exhaust samples collected during the 1979-80 and 1980-81 sampling period.

	Concentration in ng/m^3			
	Fuel Summer 1980	Average Exhaust Winter-Spring 1979-80	Fuel Spring 1981	Average Exhaust Winter-Spring 1980-81
Pyrene	1	1	1	1
Fluoranthene	2	5	4	5
Benzo(ghi)perylene*	3	3	2	4
Benzo(e)pyrene	4	2	3	2
Benzo(a)anthracene*	5	4	6	3
Naptho(1234,def)chrysene*	6	6	5	6
3-Methylcholanthrene*	7	12[a]	7	12[a]
Benzo(a)pyrene*	8	8	8	8
Benzo(k)fluoranthene	9	7	9	7
Perylene	10	11	10	11
Dibenzo(def,mno)chrysene	11	10	11	10
Benzo(rst)pentaphene*	12[a]	9	12[a]	9

[a] This PAH was not detected in the sample.

* Carcinogenic PAH

3-methylcholanthrene might decompose at the benzyl (the starred) carbons in the burning process to give benzo(a)anthracene.



In fact, it is interesting to note that the exhaust has a higher concentration of benzo(a)anthracene than one would expect from the PAH composition of the fuel, i.e., benzo(a)anthracene is more concentrated than fluoranthene in the 1979-80 and 1980-81 exhaust whereas it is significantly less concentrated than fluoranthene in both fuels. The extra benzo(a)anthracene in the exhaust may have come from the 3-methylcholanthrene in the fuel. In any case, the very good agreement between the PAH distributions in the fuel and in the exhaust is certainly consistent with the hypothesis that the PAHs in the exhaust are unburned residues of, i.e., are determined by the PAHs in the fuel. We believe that this should be pursued because burning a PAH free fuel would reduce the PAHs as well as the nitro PAHs in diesel exhaust, markedly.

Exhaust Filters and the Mine Environment

A lot of research has been done in underground mines in an effort to find ways of improving the mine environment. A good portion of this work has used PAH analyses and Ames bioassays to monitor the

changes in the concentrations of the PAHs and nitro PAHs respectively, that occur in the mine air when the mining methods or the diesel equipment have been altered. A portion of our work has involved sampling downstream from diesels working with and without a filter in the exhaust system in order to determine how the addition of these devices affects the PAH and nitro PAH[1] concentrations in the mine air.

These experiments were of interest because we believed that the PAHs were strongly adsorbed on the diesel particulate (11) and had assumed that if the particulate in the exhaust could be trapped (removed), most if not all, of the PAHs would also be removed from the exhaust. Thus, we thought that an effective filter would improve the quality of the air in the mine environment markedly. These tests were carried out in an effort to confirm this hypothesis.

A series of tests was done by sampling near a Deutz engine when it was fitted with a PTX catalytic converter and when a USBM control filter had been installed after the PTX catalytic converter in the exhaust system. This experiment was of interest because other workers have found that the USBM filter is very effective in removing the diesel particulate from the exhaust. In fact, field tests in a nickel mine near Sudbury have shown that the filter collects at least 75 percent of the particulate from a Deutz diesel and work by other scientists using a Caterpillar diesel indicates that this device removes at least 90% of the particulate (52).

The results in Table 34 were surprising because they indicated

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[1] The chemical properties of the nitro PAHs would be very similar to those of the PAHs. As a result, we believe that any device, e.g., a filter, that removes the PAHs from the exhaust will also remove the nitro PAHs, i.e., because their properties are similar we would expect a device which removes one group of compounds to also remove the other.

TABLE 34 - The effect of adding a USBM Filter to the Exhaust system of a Deutz diesel

	Concentration in ng/m^3	
	PTX only	PTX + USBM Filter
Pyrene	151	156
Fuoranthene	8.37	9.91
Benzo(a)anthracene*	12.1	8.14
Benzo(e)pyrene	12.1	25.8
Perylene	0.47	0.27
Benzo(k)fluoranthene	2.29	0.96
Benzo(a)pyrene*	2.22	0.98
Benzo(ghi)perylene*	3.46	2.65
Dibenzo(def,mno)chrysene	0.41	0.35
Naptho(1234,def)chrysene*	4.27	3.51
Benzo(rst)pentaphene*	0.53	0.53
Total PAHs	197	209
Total-pyrene	46.3	53.1
Total Carcinogens	22.6	15.8
NO_2 ppm	0.28	0.25
% CO_2	0.075	0.090

* Carcinogenic PAH

that the PAHs are equally concentrated in the mine air whether the diesel was fitted with a PTX catalytic converter or had a PTX catalytic converter and the USBM filter in the exhaust train. These preliminary results mean that either i) the filter does not reduce the PAHs when it removes the particulate, i.e., removing the particulate is not the way to reduce the PAHs in the mine air or ii) that the USBM control filter was not working on the day these samples were taken. Obviously, this test will have to be repeated before we can be certain of these results.

Because we have no reason to believe that the filter was not working on the day we collected the Hi Vol samples, we have tentatively assumed that this filter does not remove the PAHs or the nitro PAHs in the exhaust. This means that the hypothesis "that a filter that removes the diesel particulate would also remove the PAHs" is incorrect. This conclusion is surprising. We had expected that the USBM filter would be particularly effective in removing the PAHs from the exhaust because some of the diesel particulate is trapped in the filter and then the rest of the exhaust has to pass through (over) this particulate before it is released into the mine air. Because we had thought that the affinity of the PAHs for diesel exhaust was high, we had expected that any free PAHs in the exhaust would be trapped (adsorbed) when they passed over the diesel particulate in the filter.

Although this conclusion was unexpected, the results of this and other experiments (vide infra) certainly make it appear that a filter will not remove the PAHs or the nitro PAHs from the exhaust. As a result, we have revised our position and now think that adding a

simple particulate filter to the exhaust train will not remove any of the PAHs or nitro PAHs from the exhaust. This decision is based on the results of three different experiments that have shown that the affinity of PAHs for diesel particulate is much lower than we had thought. Three pertinent experiments are:-

1) The PAH levels found several feet from the diesel in a mine are approximately ten times higher than those found when the Hi Vol filter is collected right beside the exhaust outlet on the diesel. This presumably occurs because it is more difficult to trap the PAHs in the hot exhaust gases near the diesel. This may occur because i) more of the PAHs are in the vapour state and are not adsorbed on the particulate or ii) because the PAHs that are adsorbed on the Hi Vol filter are desorbed (evaporate) as more hot air is drawn over the particulate (through the filter). Whatever the cause, this result indicates that only a small portion of the PAHs are adsorbed (trapped) on the diesel particulate at high temperatures. This certainly indicates that the diesel particulate does not have a high affinity for PAHs at elevated temperatures.

2) The PAH concentrations found using long sampling periods are lower than those found when a short sampling period is used (see pages 11-18, this report). This suggests that the PAHs in the air are desorbed from the particulate on the filter when more air is drawn through the filter. This also indicates that the PAHs are not retained by the particulate even at the low temperatures, i.e., between 0 and 19°F, where these experiments were done. Obviously, this desorption of the PAHs from the Hi Vol filter would be more pronounced at the high temperatures that exist in the exhaust train of the diesel.

3) Another experiment indicates that diesel particulate does not have a high affinity for PAHs, involved placing two filters on the same Hi Vol sampler. In this experiment the PAHs on the second (back) filter were equal to 40% of the PAHs on the front filter. This means that at least 40% of the PAHs are not trapped and retained by a single Hi Vol filter. Since all of the PAHs that passed through the front filter were drawn over diesel particulate that had collected on the Hi Vol filter at a reasonably low temperature (winter mine air), the diesel particulate obviously has a low affinity for PAHs and nitro PAHs.

All three of these experiments clearly indicate that the affinity of diesel particulate for PAHs is not as high as we had thought. In fact, it appears that the affinity or trapping efficiency of diesel particulate for PAHs or nitro PAHs is fairly low. It certainly is low when the temperature is high and when large volumes of air are drawn over the particulate. Since both of these unfavourable conditions (high temperature and large air velocity) would be present in any diesel exhaust filter, it seems highly unlikely that a filter that removes the diesel particulate (soot) will remove the PAHs or the nitro PAHs from the exhaust gases. This is in fact, what we have found in the one test we have done and although the results must be confirmed, the preliminary data makes it seem that this technology will not be successful in reducing the PAH concentrations or the mutagenicity of the air around and downstream from a diesel.

In fact, removing the diesel particulate may make the contamination from the PAHs and nitro PAHs more serious in two ways. Firstly, the PAHs may stay in the mine air and travel for greater

distances through the mine if they cannot agglomerate with the diesel particulate to form heavier particles that will settle to the floor of the mine. Secondly, the PAHs and nitro PAHs that are emitted from the diesel will be in the vapour state and will obviously be respirable. Since there is no diesel particulate to pick up the PAHs and make larger (non respirable) particles, the chances of the PAHs and nitro PAHs reaching the lungs will be increased. If this occurs, the risk of contracting lung cancer is obviously increased.

In fact, two pieces of information indicate that our concerns are valid. These are, i) catalytic converters reduce the unburned hydrocarbons and probably the amount of diesel particulate that is emitted from the diesel. However, the PAH concentrations and the mutagenicity of the mine air from the diesel are also higher when a catalytic converter is used. This may occur because the soot particles that normally combine withe the PAHs and nitro PAHs in the cool mine air, are reduced when the catalyst is used. As a result, the PAHs and nitro PAHs travel for larger distances before they settle to the floor of the drift. ii) A report indicating that filters that remove the particulate increase the risk of contracting cancer, was released recently. The report states that the danger of contracting lung cancer from smoking cigarettes is enhanced when a filter is on the cigarette. In a cigarette without a filter, the PAHs in the cigarette smoke become adsorbed on the smoke particles and are too large to reach the lower portions (alveoli) of the lung. As a result, the smoke particles and the PAHs are removed by the mucociliary escalator and very few of the carcinogenic PAHs reach the alveolar region of the lung. If the particulate is removed from the cigarette smoke with a filter, the PAHs are not trapped but pass through the

filter in the vapour state. As a result, much greater concentrations of PAHs reach the alveolar region of the lung where they are deposited and can induce lung cancer. Thus, an effective filter increases the danger of contracting lung cancer from the PAHs given off by the cigarette. This is exactly the effect suggested above. Thus, it appears that the filters may not improve the work environment but may worsen it substantially.

CONCLUSION

Several experiments have shown that the PAHs are not collected quantitatively on a Hi Vol filter. In fact, significant amounts of PAHs are lost (desorbed) when air is drawn over the particulate on the filter (through the Hi Vol). The losses which increase linearly with sampling time are large, e.g., 63% of the PAHs collected on the filter are desorbed (lost) when the sample is collected for 24 hours. Moreover, a significant portion of the PAHs in the mine air are not trapped by a single filter, i.e., the PAHs on a back-up (second) filter are equal to 40% of the PAHs on the first (front) filter. These results are important because they demonstrate i) that the PAHs do not have a high affinity for diesel exhaust and ii) that the Hi Vol method of sampling is far from quantitative. The collection efficiency is certainly below 60% and in fact it probably is below 25%. This means that the PAH concentration and mutagenicity of the mine air are much higher than those found by analyzing Hi Vol samples.

Other work has shown that the PAH concentrations in the air above ground and in the fresh air raises underground vary markedly from day to day. This means that background PAH levels are required at each test site if the effect of a particular mining operation or piece of equipment is to be determined with any certainty.

PAH analyses have shown that the PAH concentrations are approximately 30% higher in the fresh air raises than they are at the surface during the spring, summer and fall months. In the winter on

the other hand, the PAHs in the fresh air raises are only 20% as concentrated as they are on the surface. This presumably occurs because some of the PAHs are burned when the intake air is heated before it is taken into the mine.

PAH analyses have also been used to test some of the hypotheses presented in the 1980-81 report. For example, these studies have confirmed that the PAHs settle out of the air very quickly in humid, hardrock (nickel and uranium) mines but travel for very long distances through dry salt mines. Other work has shown that PAHs settle out more quickly when the drifts are irregular, i.e., bends and curves. These and other experiments have confirmed that the PAH concentrations are indeed, related to drift size. Moreover, these studies have suggested that the PAHs are removed very slowly from mines with large drifts. This conclusion is supported by the observation that the concentrations of the PAHs and nitro PAHs (the mutagenicity) undergo dramatic increases very rapidly, i.e., in minutes when the ventilation is not adequate in a mine with large drifts. These discoveries are important because they demonstrate that the amount of ventilation in a mine should be determined by i) drift size, ii) the type of ore mined, iii) the mine layout and iv) the amount of diesel activity in the mine. Obviously, more than 100 cfm/brake horsepower of ventilation is required in dry salt mines with large, straight drifts if the PAHs and nitro PAHs are to be removed from the work site quickly.

Ames Salmonella bioassays have shown that the mutagenicity of the diesel exhaust samples is almost entirely due to the nitro PAHs which are formed from NO_2 and the PAHs in the engine and/or exhaust

system of the diesel. In addition, these studies have shown that the PAH concentration and the mutagenic response (nitro PAHs) are greater when a catalytic converter is added to a diesel's exhaust system. Although a PTX catalyst increases both the PAHs and the mutagenicity of the exhaust significantly, the effect is small in comparison to that observed when a Dieseler III catalyst is used. In fact, the air downstream from a diesel with a Dieseler III catalytic converter is between 15 and 125 times more mutagenic and has up to 5 times more PAHs than the air downstream from an engine with no exhaust treatment devices. Since the Dieseler III catalyst increases the concentrations of the carcinogenic PAHs and the mutagenic nitro PAHs in the exhaust markedly, this catalyst should be removed from the diesels used in underground mines. In fact, the disadvantages of using catalytic converters in the exhaust train seem to outweigh the advantages. These devices increase PAH concentrations, the nitro PAH concentrations (the mutagenicity), the sulfuric acid levels, probably the NO_2 and aldehyde levels and certainly the cost. The CO and hydrocarbons they remove from the exhaust do not constitute a problem from a health point of view.

Studies in a mine with high NO_2 levels indicate that the nitro PAHs are generated in the engine and/or exhaust system and not in the mine environment or on the filter as a sampling artifact. The results also indicate that the PAH concentration and mutagenicity of the exhaust depend on the load on the engine and the NO_2 levels. This is important because it indicates that engines and equipment will either have to be tested at several different loads and environments or that a standard duty cycle with different loads and environments will have

to be developed.

Finally, very low levels of nitro PAHs and very high concentrations of PAHs have been found in the exhaust from Detroit diesels. However, we do not know whether it would be better to use a Detroit diesel which emits very little of the mutagenic nitro PAHs and high concentrations of the carcinogenic PAHs or whether one should use a Deutz or Caterpillar diesel that gives off lower levels of both nitro PAHs and PAHs.

Ames bioassays and PAH analyses of Hi Vol samples collected downstream from blasting and rock drilling operations in a non dieselized mine have shown that both of the processes add large amounts of PAHs to the mine environment. In fact, the PAH concentrations and average revertants/m^3 downstream from even small blasts using Amex (ammonium nitrate-diesel fuel) explosive are particularly high, i.e., they are much higher than those found near any other mining operation. Although the oil mists also contain large amounts of PAHs, these samples are not mutagenic, presumably because the oil does not contain any nitro PAHs. Work to reduce the PAHs and nitro PAHs generated by blasting and drilling operations in the mine environment should be undertaken in the near future.

Work completed during the course of this study has strengthened our belief that the PAHs in the exhaust (mine air) are an unburned residue of (determined by) the PAHs in the fuel. This means that any problems arising from the PAHs and/or the nitro PAHs in underground mines could be greatly reduced if a low PAH fuel were burned in the diesel. This would obviously reduce the PAHs in the exhaust markedly and since the nitro PAHs are formed from the PAHs and NO_2, it would

also reduce or even eliminate the nitro PAHs (the mutagenicity) in the exhaust.

Finally, preliminary work suggests that filters which remove diesel particulate (soot) from the exhaust will not reduce the concentrations of the PAHs or nitro PAHs significantly. This occurs because the PAHs have a low affinity for diesel particulate at the high temperatures and high air velocities that are present in the exhaust system. Thus, the PAHs and nitro PAHs would pass through the filter and be expelled into the mine air. Since the PAHs and the nitro PAHs may travel for larger distances through the mine when they cannot combine with the diesel particulate at mine temperatures to form heavier particles that will settle to the floor of the drift, removing the soot with a filter may increase the problems associated with the presence of PAHs and nitro PAHs in the mine air.

EXPERIMENTAL

No new procedures were used or developed during the course of this work.

The procedures used to collect the samples for PAH analysis and the Ames bioassay have been described previously (11).

The methods used in doing the quantitative analysis of the thirteen PAHs and the five strain Salmonella bioassay are also described in detail in the previous report (11). The procedure used to purify the oil mist samples for Ames and PAH analysis is described in reference 21.

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